

Organic Reactions

VOLUME 13

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PREFACE TO THE SERIES

In the course of nearly every program of research in organic chemistry the investigator finds it necessary to use several of the better-known synthetic reactions. To discover the optimum conditions for the application of even the most familiar one to a compound not previously subjected to the reaction often requires an extensive search of the literature, even then a series of experiments may be necessary. When the results of the investigation are published, the synthesis, which may have required months of work, is usually described without comment. The background of knowledge and experience gained in the literature search and experimentation is thus lost to those who subsequently have occasion to apply the general method. The student of preparative organic chemistry faces similar difficulties. The textbooks and laboratory manuals furnish numerous examples of the application of various syntheses, but only rarely do they convey an accurate conception of the scope and usefulness of the processes.

For many years American organic chemists have discussed these problems. The plan of compiling critical discussions of the more important reactions thus was evolved. The volumes of *Organic Reactions* are collections of chapters each devoted to a single reaction, or a definite phase of a reaction, of wide applicability. The authors have had experience with the processes surveyed. The subjects are presented from the preparative viewpoint, and particular attention is given to limitations, interfering influences, effects of structure, and the selection of experimental techniques. Each chapter includes several detailed procedures illustrating the significant modifications of the method. Most of these procedures have been found satisfactory by the author or one of the editors, but unlike those in *Organic Syntheses* they have not been subjected to careful testing in two or more laboratories. When all known examples of the reaction are not mentioned in the text, tables are given to list compounds which have been prepared by or subjected to the reaction. Every effort has been made to include in the tables all such compounds and references, however, because of the very nature of the reactions discussed and their frequent use as one of the several steps of syntheses in which not all of the intermediates have been isolated, some instances may well have been missed. Nevertheless, the investigator will be able

to use the tables and their accompanying bibliographies in place of most or all of the literature search so often required.

Because of the systematic arrangement of the material in the chapters and the entries in the tables, users of the books will be able to find information desired by reference to the table of contents of the appropriate chapter. In the interest of economy the entries in the indices have been kept to a minimum, and, in particular, the compounds listed in the tables are not repeated in the indices.

The success of this publication, which will appear periodically, depends upon the cooperation of organic chemists and their willingness to devote time and effort to the preparation of the chapters. They have manifested their interest already by the almost unanimous acceptance of invitations to contribute to the work. The editors will welcome their continued interest and their suggestions for improvements in *Organic Reactions*.

CHAPTER 1

HYDRATION OF OLEFINS, DIENES, AND ACETYLENES VIA HYDROBORATION

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Purdue University

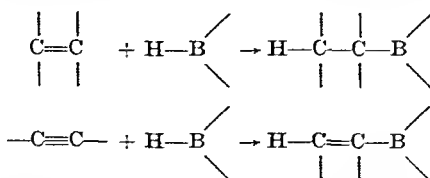
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INTRODUCTION

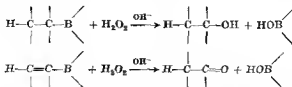
The hydroboration of olefins, dienes, and acetylenes involves the addition of a boron-hydrogen bond to the carbon-carbon multiple bond.^{1,2} This



¹ Brown and Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956); **81**, 6423, 6428 (1959); *J. Org. Chem.*, **22**, 1136 (1957).

² Brown and Zweifel, *J. Am. Chem. Soc.*, **81**, 1512 (1959); **83**, 3834 (1961).

reaction provides a new convenient route to the corresponding organoboranes and makes them readily available as intermediates in organic synthesis. One of the important reactions which the organoboranes undergo is the rapid and essentially quantitative oxidation with alkaline hydrogen peroxide.



The hydroboration of olefins involves a *cis* addition of the boron-hydrogen bond, the boron atom becoming attached to the less substituted of the two olefinic carbon atoms of the double bond. Furthermore the oxidation occurs with retention of configuration, placing the hydroxyl group at the precise position occupied by the boron atom in the initial organoborane. Both the hydroboration and the oxidation reactions appear to be free of the carbon skeleton rearrangements that occasionally accompany other hydration procedures. As a result, hydroboration followed by oxidation with alkaline hydrogen peroxide has become an important new synthetic method for the anti-Markownikoff, *cis* hydration of double bonds.

This chapter surveys the available information on the hydration of olefins, dienes, acetylenes, and their derivatives by the hydroboration-oxidation procedure.*

Early observations on the reaction of diborane with olefins indicated that the reaction required elevated temperatures and long reaction periods³ and did not provide a convenient route to organoboranes. Later it was observed that anhydrous aluminum chloride enhanced the reducing power of sodium borohydride to the point where the reagent at room temperature readily reduced substances such as nitriles and esters, groups which are normally resistant to sodium borohydride itself.⁴ Even more unexpected was the observation that olefins reacted with the reagent, utilizing one B-H equivalent per molecule of olefin and forming an organoborane.⁴

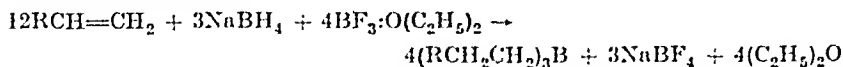


* Another survey is to be found in an article by Brown, *Tetrahedron*, 12, 117 (1951), and a detailed treatment of the hydroboration reaction and of the synthetic applications of the resulting organoboranes is given by Brown, *Hydroboration*, W. A. Benjamin, New York, 1962.

³ Hurd, *J. Am. Chem. Soc.*, 70, 2053 (1948); Stone and Emelous, *J. Chem. Soc.*, 1950, 2755; Whatley and Pease, *J. Am. Chem. Soc.*, 76, 835 (1954); Stone and Graham, *Chem. & Ind. (London)*, 1955, 1861.

⁴ Brown and Subba Rao, *J. Am. Chem. Soc.*, 75, 2582 (1953); 81, 6423 (1959).

This discovery led to the search for alternative procedures for hydroboration. It was found that hydroboration could readily be achieved by treating an olefin with sodium borohydride and boron trifluoride in an appropriate solvent.



It was also discovered that, contrary to the impression given by the earlier reports, diborane itself adds rapidly and quantitatively to olefins in ether solvents.¹

$$6\text{RCH}=\text{CH}_2 + \text{B}_2\text{H}_6 \rightarrow 2(\text{RCH}_2\text{CH}_2)_3\text{B}$$

The reaction appears to be as general as the addition of hydrogen or bromine to multiple carbon-carbon bonds.

Johnson and Van Campen had noted that alkaline hydrogen peroxide effected a complete dealkylation of tri-*n*-butylborane and related organoboranes to form alcohols and boric acid.⁵ A detailed study of this reaction revealed that the oxidation is essentially quantitative at 25°, that the solvents utilized for the hydroboration do not interfere with the oxidation and hence the reaction can be performed without isolating the organoborane, and that the reaction is of very wide generality.⁶

The subject matter of this chapter is limited to hydroboration-oxidation as a specific combination for the hydration of multiple carbon-carbon bonds under mild conditions. It may be noted, however, that organoboranes undergo protonolysis in the presence of carboxylic acids, providing a non-catalytic means of hydrogenating multiple carbon-carbon bonds.⁷ Organoboranes also undergo coupling on treatment with alkaline silver nitrate, and this reaction provides a new synthesis for carbon-carbon bonds.⁸

HYDROBORATION OF OLEFINS

As a result of the developments outlined above, two convenient procedures are available for the hydroboration of olefins under mild conditions: (1) treatment of a mixture of the unsaturated compound and an alkali metal borohydride in a suitable solvent with boron trifluoride etherate (or other acid), and (2) external generation of diborane followed by its reaction with the unsaturated compound in an appropriate solvent. Each of these procedures possesses advantages that will lead to its selection for specific reactions. Both procedures are described in the section on Experimental Procedures.

⁵ Johnson and Van Campen, *J. Am. Chem. Soc.*, **60**, 121 (1938).

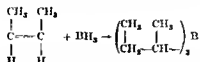
⁶ H. C. Brown, C. H. Snyder, B. C. Subba Rao, and G. Zweifel, to be published.

⁷ Brown and Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

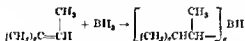
⁸ Brown, Hébert, and Snyder, *J. Am. Chem. Soc.*, **83**, 1001 (1961); Brown and Snyder, *ibid.*, **83**, 1001 (1961); Brown, Verbrugge, and Snyder, *ibid.*, **83**, 1002 (1961).

Scope and Stoichiometry

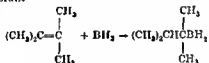
The hydroboration reaction has been applied to a large number of olefins of widely different structures. In practically all cases the reaction proceeds simply and rapidly. Only the most hindered olefins exhibit any resistance to addition. Simple olefins commonly utilize all the hydrogen atoms of diborane and form the trialkylborane



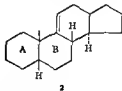
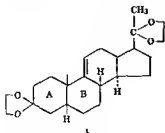
However, trisubstituted olefins, such as 2-methyl-2-butene and 1-methylcyclohexene, utilize only two of the three hydrogen atoms of the borane group forming a dialkylborane



Further reaction to form a trialkylborane is very slow at room temperature. Finally, tetrasubstituted olefins, such as tetramethylethylene, react rapidly to utilize only one hydrogen atom of the borane group and form the monoalkylborane



Up to the present time only two olefins, the steroids 1 and 2 (Refs 9 and 10, respectively), have been reported not to undergo hydroboration



* Wechter, *Chem. & Ind. (London)*, 1959, 294

¹⁰ Nassim and Sondheimer, *Chem. & Ind. (London)*, 1960, 400

On the other hand, the analogous compounds with the A/B-*trans* junction do undergo hydroboration.

The stoichiometry of the hydroboration reaction for a number of representative olefins is summarized in Table I.

TABLE I

STOICHIOMETRY OF HYDROBORATION OF REPRESENTATIVE OLEFINS^{1,11}

	Acyclic Olefins	Cyclic Olefins
(a)	3 Olefin + BH ₃ $\xrightarrow{20^\circ}$ Trialkylborane, R ₃ B	
	2-Methyl-1-butene	Cyclopentene
	3-Methyl-1-butene	Cyclohexene
	1-Hexene	Cycloheptene
	2-Hexene	Norbornene
	3-Hexene	β -Pinene
	4-Methyl-2-pentene	
	3,3-Dimethyl-1-butene	
	2,4,4-Trimethyl-1-pentene	
	Styrene	
	α -Methylstyrene	
	1-Tetradecene	
(b)	2 Olefin + BH ₃ $\xrightarrow{20^\circ}$ Dialkylborane, R ₂ BH	
	2-Methyl-2-butene	1-Methylcyclopentene
	4,4-Dimethyl-2-pentene	1-Methylcyclohexene
	2,4,4-Trimethyl-2-pentene	α -Pinene
(c)	1 Olefin + BH ₃ $\xrightarrow{20^\circ}$ Monoalkylborane, RBH ₂	
	2,3-Dimethyl-2-butene	1,2-Dimethylcyclopentene
	2,2,5,5-Tetramethyl-3-hexene ¹²	1,2-Dimethylcyclohexene

Directive Effects¹³

The oxidation of an organoborane to an alcohol by alkaline hydrogen peroxide is essentially quantitative and proceeds without rearrangement. Consequently, the structure of the alcohol formed serves to locate the position of the boron atom in the organoborane.

Terminal olefins, RCH=CH₂, give predominantly addition of the boron atom to the terminal carbon atom (93–94%). Thus hydroboration of 1-hexene yields an organoborane which, upon oxidation with alkaline hydrogen peroxide, is converted to a mixture composed of 94% 1-hexanol and 6% 2-hexanol. Similar results are observed with 1-butene, 1-pentene,

¹¹ Brown and Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

¹² Logan and Flautt, *J. Am. Chem. Soc.*, **82**, 3446 (1960).

¹³ Brown and Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960).

and 1-octene, establishing the predominantly *anti*-Markownikoff direction of addition.¹ Branching of the alkyl chain as in 3-methyl-1-butene, 3,3-dimethyl-1-butene, and 4,4-dimethyl-1-pentene makes no essential difference in the direction of addition.

The presence of an alkyl substituent in the 2 position increases the directive effect. The boron atom adds to the terminal position of olefins such as 2-methyl-1-butene to the extent of 99%.

TABLE II
DIRECTIVE EFFECTS IN THE HYDROBORATION OF
TERMINAL OLEFINS AT 20°

Olefin	Alcohol	Distribution, ^a %
	1-ol	2-ol
1-Butene	93	7
1-Pentene	94	6
2-Methyl-1-butene	99	1
3-Methyl-1-butene	94	6
1-Hexene	94	6
3,3-Dimethyl-1-butene	94	6
4,4-Dimethyl-1-pentene	93	7
Styrene	80	20
p-Chlorostyrene	65	35
2,4,4-Trimethyl-1-pentene	99	1
α -Methylstyrene	100	Trace
p-Methylstyrene	82	18
p-Methoxystyrene	91	9
Allylbenzene	90	10

^a The yields by gas-liquid partition chromatography were $90 \pm 10\%$.

The addition to styrene is less selective; 80% of the boron becomes attached to the terminal position and 20% to the secondary carbon atom. Moreover, the direction of addition is strongly modified by substituents in the *para* position of the aromatic nucleus.

The results are summarized in Table II.

The data in Table II—specifically the facts that ethylene, isopropyl-ethylene, and *t*-butylethylene give 93%, 94%, and 94%, respectively, of primary alcohol—clearly show that an increase in the bulk of the alkyl group attached to the double bond does not influence the direction of addition. These results argue against steric control of the direction of addition. The marked influence of *para* substituents on the direction of addition to styrene supports the contention that the direction of addition is controlled primarily by electronic factors.

Dialkyl ethylenes, $RCH=CHR'$, such as 2-pentene and 2-hexene, undergo addition to place the boron atom in approximately equal

amounts on the 2- and 3-carbon atoms. This is true even for molecules such as *trans*-4-methyl-2-pentene and *trans*-4,4-dimethyl-2-pentene, where the two alkyl groups differ markedly in their steric requirements. Only in *trans*-1-phenylpropene, where the phenyl group is opposed to a methyl group, is a marked directive effect indicated; the boron atom becomes attached to the carbon atom holding the phenyl substituent to the extent of 85% (Table III).

TABLE III
DIRECTIVE EFFECTS IN THE HYDROBORATION OF
INTERNAL OLEFINS AT 20°

Olefin	Alcohol Distribution, ^a %	
	2-ol	3-ol
<i>cis</i> -2-Pentene	55	45
<i>trans</i> -2-Pentene	51	49
2-Methyl-2-butene ^b	98 ^c	2
<i>cis</i> -2-Hexene	50	50
<i>trans</i> -2-Hexene	46	54
<i>trans</i> -4-Methyl-2-pentene	57	43
<i>trans</i> -4,4-Dimethyl-2-pentene ^b	58	42
2,4,4-Trimethyl-2-pentene ^b	2	98 ^d
<i>trans</i> -1-Phenylpropene	85 ^e	15 ^f

^a The yields by gas-liquid partition chromatography were $90 \pm 10\%$.

^b The addition yields a dialkylborane.

^c The product is 3-methyl-2-butanol.

^d The product is 2,2,4-trimethyl-3-pentanol.

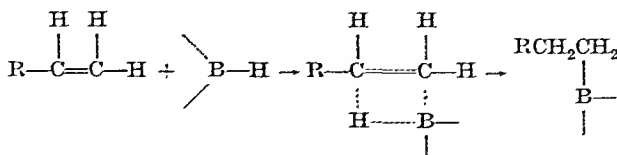
^e The product is 1-phenyl-1-propanol.

^f The product is 1-phenyl-2-propanol.

Trisubstituted olefins, $R_2C=CHR$, such as 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene, add the boron atom predominantly at the less substituted ethylenic carbon atom.

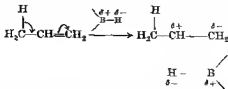
The data are summarized in Table III

Diborane undergoes *cis* addition to cyclic olefins and to acetylenes, which will be discussed later. Consequently, the addition very likely involves a four-center transition state.

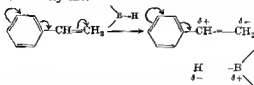


The boron-hydrogen bond is presumably polarized, the hydrogen having some hydridic character. The addition of the boron atom to the terminal position is then readily understood on the basis of the electronic shifts

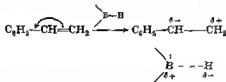
generally assumed in order to account for the normal ionic addition to propylene.



A similar rationalization explains the addition of the boron atom to the terminal position of styrene.



It is generally recognized that a phenyl group can supply electrons to an electron-deficient center or serve as an electron sink. This provides a simple explanation for the increased substitution in the α position observed in styrene.



Electron-withdrawing substituents, such as *p*-chloro, should stabilize and electron-supplying substituents, such as *p*-methoxy, should destabilize such a transition state. This conclusion is in accord with the influence of the *p* chloro and the *p*-methoxyl group on the hydroboration of substituted styrenes (Table II)

Little quantitative information is available concerning the influence of other substituents on the direction of the addition reaction. It is evident that major effects will be encountered. Trimethylvinylsilane undergoes hydroboration to place 37% of the boron atoms at the secondary position¹⁴ as compared to 6% for 3,3-dimethyl-1-butene.¹⁵

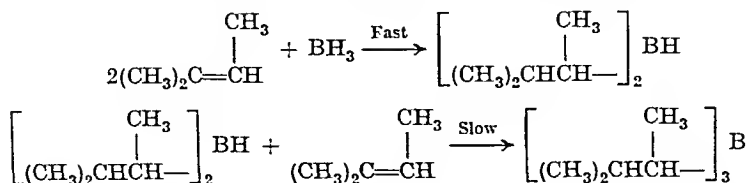
Bis-(3-methyl-2-butyl)borane as a Selective Hydroborating Agent¹⁵

It was pointed out earlier that highly substituted olefins, such as 2-methyl-2-butene, undergo hydroboration rapidly to the dialkylborane

¹⁴ Seyferth, *J. Inorg. Nucl. Chem.*, **7**, 152 (1958).

¹⁵ Brown and Zweifel, *J. Am. Chem. Soc.*, **83**, 1241 (1961).

stage, further reaction to the trialkylborane stage being relatively slow.



The slowness of the last stage, in contrast to the high speed with which other olefins form the trialkylboranes, is presumably a result of the large steric requirement of the intermediate dialkylborane. It therefore

TABLE IV
DIRECTIVE EFFECTS IN THE HYDROBORATION OF UNSYMMETRICAL
OLEFINS WITH DIBORANE AND WITH BIS-(3-METHYL-2-BUTYL)BORANE

Olefin	Hydroborating Agent	Temp., °C.	Time, hr.	Alcohol Distribution, %		
				1-ol	2-ol	3-ol
1-Hexene	Diborane	25	1	94	6	
	R ₂ BH ^a	0	1	99	1	
<i>cis</i> -4-Methyl-2-pentene	R ₂ BH ^a	25	12		97	3
<i>trans</i> -4-Methyl-2-pentene	Diborane	25	1		57	43
	R ₂ BH ^a	25	12		95	5
Styrene	Diborane	25	1	80	20	
	R ₂ BH ^a	25	2	98	2	
<i>p</i> -Methoxystyrene	Diborane	25	1	91	9	
	R ₂ BH ^a	25	2	98	2	

^a R₂BH is $\left[(\text{CH}_3)_2\text{CHCH}- \right]_2 \text{BH}$.

appeared that this dialkylborane might exhibit an enhanced sensitivity to the steric requirement of the substituents on double bonds of other olefins and thereby exert a steric influence on the direction of hydroboration.

The reagent, bis-(3-methyl-2-butyl)borane, reacted rapidly with 1-hexene, and oxidation of the product yielded 1-hexanol in an isomeric purity of at least 99%, in contrast to the 94% isomeric purity realized with diborane itself. Similarly, styrene yielded less than 2% of the secondary alcohol, in contrast to 20% formed in the corresponding reaction with diborane. Finally, *cis*-4-methyl-2-pentene gave 97% of the less hindered isomer, 4-methyl-2-pentanol.

The experimental data are summarized in Table IV.

In these studies the ease with which different olefins reacted with bis-(3-methyl-2-butyl)borane was found to vary enormously. Thus the reaction with 1-hexene was complete in a matter of minutes at 0°, whereas

internal olefins reacted much more slowly, cyclopentene reacting faster than *cis*-2-hexene and the latter reacting considerably faster than cyclohexene. *cis*-2-Hexene also reacted considerably faster than the *trans* isomer. Trisubstituted olefins, such as 2-methyl-2-butene and 1-methylcyclohexene, reacted very slowly.

The results may be expressed in the following series of relative rates of reaction. 1-hexene \geq 3-methyl-1-butene $>$ 2-methyl-1-butene $>$ 3,3-dimethyl-1-butene $>$ *cis*-2-hexene \geq cyclopentene $>$ *trans*-2-hexene $>$ *trans*-4-methyl-2-pentene $>$ cyclohexene \geq 1-methylcyclopentene $>$ 2-methyl-2-butene \geq 1-methylcyclohexene \geq 2,3-dimethyl-2-butene

The differences in reactivities are quite large and can be utilized for the selective hydroboration of a more reactive olefin in the presence of a less reactive one. Thus treatment of a mixture of 1-pentene and 2-pentene with a controlled quantity of bis-(3-methyl-2-butyl)borane yielded pure 2-pentene. Similar treatment of a mixture of 1-hexene and cyclohexene afforded essentially pure cyclohexene, while an equimolar mixture of cyclopentene and cyclohexene gave a product containing only minor amounts of the more reactive cyclopentene. A commercial mixture of *cis*- and *trans*-2-pentene (18% *cis* and 82% *trans*) with the reagent gave a product that contained more than 97% of the *trans* isomer.

In contrast to the results achieved with acyclic olefins, no significant directive effect was noted in the hydroboration of 3-methylcyclopentene, 3-methylcyclohexene, or 3,3-dimethylcyclohexene.¹¹

In a rigid cyclic system, selective reaction was observed. Treatment of 1-cholestene with bis-(3-methyl-2-butyl)borane resulted in the predominant formation of cholestan-2 α -ol, in contrast to the nearly 1:1 mixture of cholestan-1 α -ol and cholestan-2 α -ol obtained with diborane.¹²

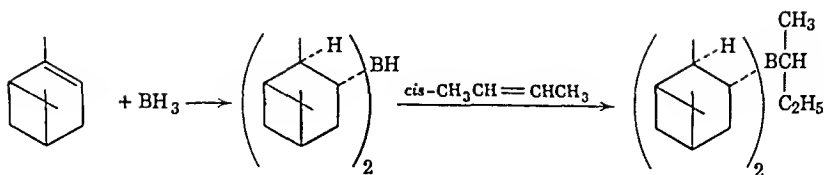


Asymmetric Synthesis

The remarkable selectivity of a dialkylborane in hydroboration is further illustrated by the conversion of olefins to optically active alcohols.¹⁷ Hydroboration of α -pinene ($[\alpha]_D + 47^\circ$) gives diisopinocampheylborane.¹¹ This reagent was utilized for the hydroboration of *cis*-2-butene, *cis*-3-hexene, and norbornene. Oxidation of the resulting organoborane with

¹² Sandheimer and Nussim, *J. Org. Chem.*, **28**, 830 (1963)

¹⁷ Brown and Zweifel, *J. Am. Chem. Soc.*, **83**, 486 (1961)

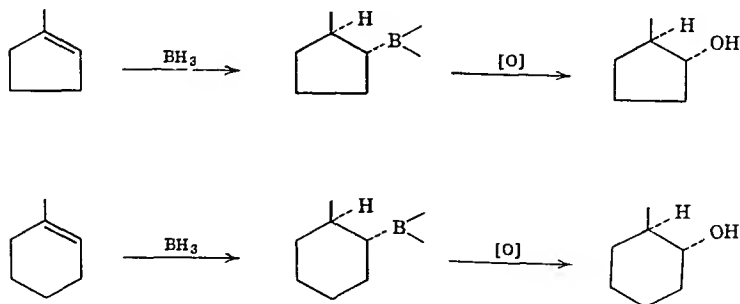


alkaline hydrogen peroxide produced the corresponding alcohols in optical purities of 70–90%. It is noteworthy that the alcohols obtained from the hydroboration of acyclic *cis*-olefins with the diisopinocampheylboranes derived from (+) or (–) α -pinene have the R and S configurations, respectively. *trans*-Olefins and hindered olefins react only slowly with diisopinocampheylborane.

Negligible racemization of the asymmetric organoborane was observed when it was kept for several hours at room temperature.¹⁸

Stereochemistry

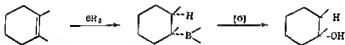
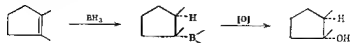
The hydroboration of cyclic olefins provides a means of determining the stereochemistry of the reaction.¹¹ Thus the hydroboration of 1-methylcyclopentene and 1-methylcyclohexene, followed by oxidation with alkaline hydrogen peroxide, results in the formation of almost pure *trans*-2-methylcyclopentanol and *trans*-2-methylcyclohexanol, respectively. The available evidence indicates that the hydrogen peroxide oxidation proceeds with retention of configuration. Consequently, the hydroboration must involve a *cis* addition of the hydrogen-boron bond to the olefinic linkage.



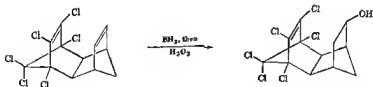
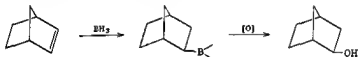
The products of these reactions are the thermodynamically more stable isomers. However, thermodynamic stability of the product cannot be

¹⁸ H. C. Brown, N. R. Ayyangar and G. Zweifel, to be published.

the controlling factor in the reaction because the hydroboration of 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene produces the thermodynamically less stable isomers, pure *cis*-1,2-dimethylcyclopentanol and *cis*-1,2-dimethylcyclohexanol, respectively



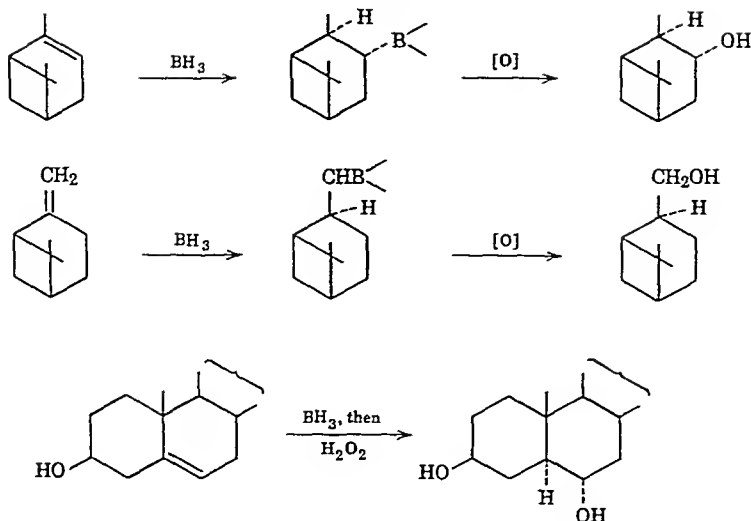
The hydroboration of norbornene proceeds to give *exo*-norborneol almost exclusively. Similarly the hydroboration-oxidation of isodrin occurs from the less hindered side.^{19,20}



The generalization that hydroboration proceeds by *cis* addition from the less hindered side of the double bond is now supported by a considerable number of observations. α -Pinene is readily converted to isopinocampheol, β -pinene to *cis* myrtanol, and cholesterol to cholestane-3 β ,6 α -diol.⁹

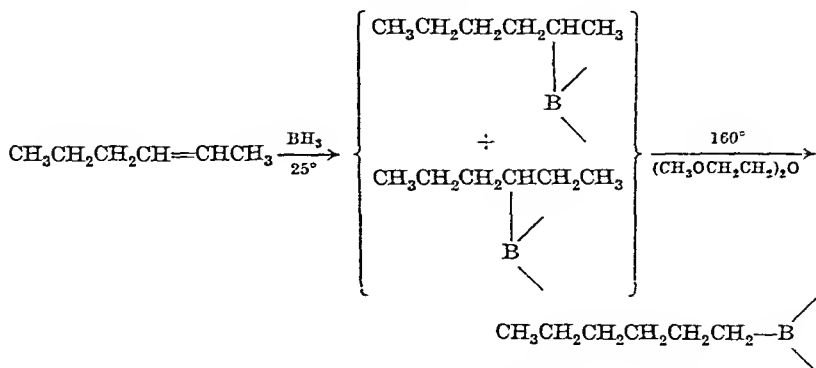
¹⁹ Cookson and Crundwell, *Chem. & Ind. (London)*, 1959, 703. Bard, Cookson, and Crundwell, *J. Chem. Soc.*, 1961, 4809.

²⁰ Bruck, Thompson, and Winsten, *Chem. & Ind. (London)*, 1960, 405.



Isomerization of Organoboranes

A simple synthetic route to primary organoboranes involves the isomerization of organoboranes derived from internal olefins. Secondary and tertiary organoboranes, synthesized by means of the Grignard reaction, slowly isomerize at 200–215° to yield primary organoboranes.²¹ The isomerization is far more rapid under hydroboration conditions. Thus tri-2-hexylborane is almost completely isomerized to tri-*n*-hexylborane in one hour at 160° in diglyme solution.^{1,22}



²¹ Hennion, McCusker, Ashby, and Rutkowski, *J. Am. Chem. Soc.*, 79, 5190 (1957).

²² Brown and Subba Rao, *J. Am. Chem. Soc.*, 81, 6434 (1959).

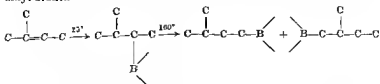
The small quantities of excess diborane produced in the hydroboration stage markedly catalyze the isomerization.²³ Typical results are summarized in Table V.

TABLE V
ISOMERIZATION OF ORGANOBORANES AT 160°²³

Olefin	Location of the Boron ^a					
	Initially at 25°, %		After 1 hr. at 160°, %			
	2	3	1	2	3	4
$\begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} \\ \text{(1) (2) (3) (4)} \\ \text{C} - \text{C} = \text{C} - \text{C} - \text{C} \\ \text{C} - \text{C} = \text{C} - \text{C} - \text{C} - \text{C} \end{array}$	52	48	93	4	1	
	46	54	91	6	3	
$\begin{array}{c} \text{C} \quad \quad \text{C} \\ \quad \quad \\ \text{C} - \text{C} = \text{C} - \text{C} - \text{C} \\ \quad \quad \\ \quad \quad \text{C} \end{array}$	1	99	97	1	2	
$\begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} = \text{C} - \text{C} - \text{C} \\ \quad \quad \\ \quad \quad \text{C} \end{array}$	57	43	96	2	2	
$\begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} = \text{C} - \text{C} \end{array}$	98	2	52	1	Tr.	47
$\text{C} - \text{C} = \text{C} - \text{C}_6\text{H}_5$	15	85	76	10	14	

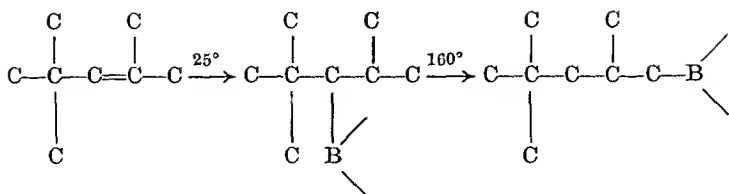
^a The numbers indicate the position of the boron atom, counting from the left-hand end of the chain.

The results indicate that the boron atom not only moves readily down a straight chain, but also encounters no difficulty in moving past a single alkyl branch.

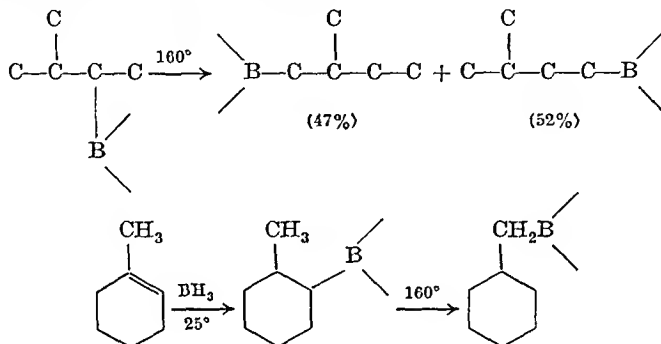


However, under the mild conditions generally used, the boron atom does not migrate past a double branch.

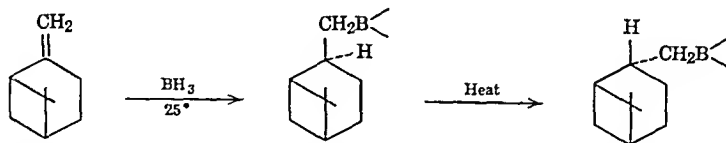
²³ Brown and Zweifel, *J. Am. Chem. Soc.*, **82**, 1504 (1960), *ibid.*, to be published.



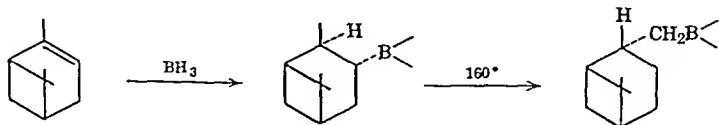
In these isomerizations, the boron atom migrates preferentially to the least hindered position in the molecule.



It is noteworthy that hydroboration of β -pinene yields the *cis*-organoborane.¹¹ However, on heating, the *cis*-organoborane is converted to the more stable *trans* derivative.^{24,25}



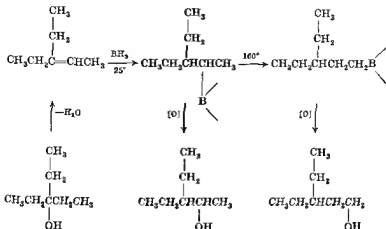
Moreover, the *trans* derivative is obtained from the hydroboration of α -pinene followed by isomerization.²⁴



The versatility of the hydroboration reaction when coupled with thermal isomerization is illustrated by the following transformations, all of which proceed readily in yields of approximately 90%.

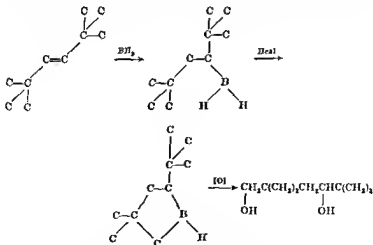
²⁴ H. C. Brown, M. V. Bhatt, and G. Zweifel. Unpublished research.

²⁵ Braun and Fisher, *Tetrahedron Letters*, No. 21, 9 (1960).



Thermal Cyclization of Organoboranes

Certain organoboranes cyclize at elevated temperatures^{12,26-28}. Thus the monoalkylborane derived from *trans*-di-*t*-butylethylene loses hydrogen above 100° to form a cyclic organoborane. Oxidation of this cyclic product gives 2,2,5,5-tetramethyl-1,4-hexanediol.¹²

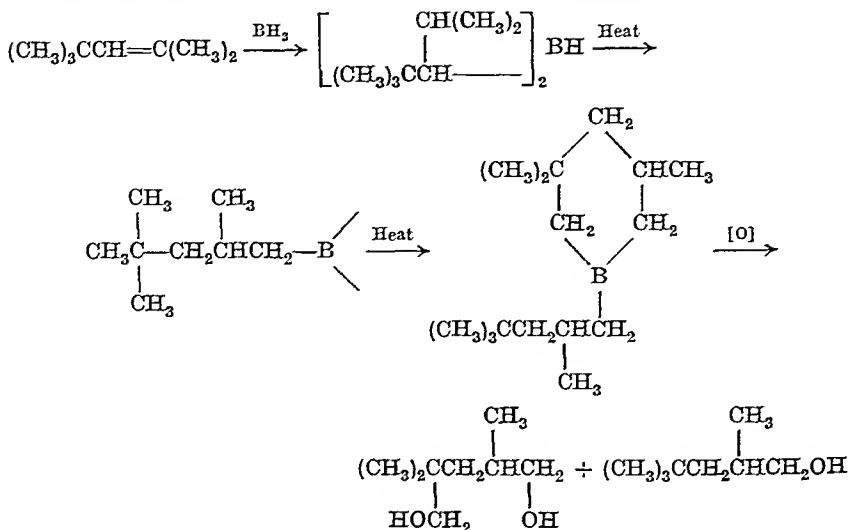


¹² Winternitz and Carotta, *J. Am. Chem. Soc.*, **82**, 2420 (1960).

²⁶ Kötter and Rotermund, *Angew. Chem.*, **72**, 126 (1960); **72**, 563 (1960).

²⁸ H. C. Brown, K. J. Murray, and G. Zweifel. Unpublished research.

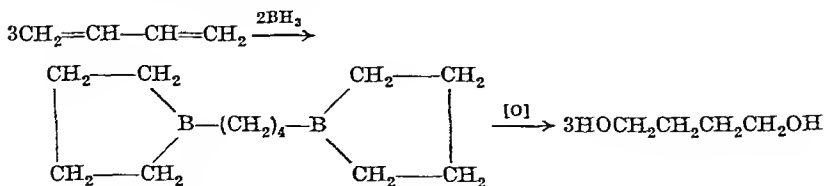
Similarly, at 160° in refluxing diglyme, bis-(2,4,4-trimethyl-1-pentyl)-borane undergoes cyclization. Oxidation of the product yields 2,4,4-trimethyl-1,5-pentanediol and 2,4,4-trimethyl-1-pentanol.²⁸



HYDROBORATION OF DIENES

Hydroboration with Diborane

Dihydroboration of dienes followed by oxidation of the organoborane provides a route to diols.²⁹⁻³² 1,3-Butadiene is transformed into a 4:1 mixture of 1,4- and 1,3-butanediol. Köster has assigned a cyclic structure to the organoborane derived from 1,3-butadiene.³⁰



By similar procedures 1,5-hexadiene²⁹ and cyclopentadiene^{31,32} are converted to 1,6-hexanediol and *trans*-1,3-cyclopentanediol, respectively.

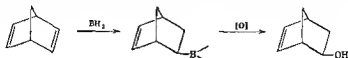
²⁹ Brown and Zweifel, *J. Am. Chem. Soc.*, **81**, 5832 (1959); Zweifel, Nagase, and Brown, *ibid.*, **84**, 183 (1962).

³⁰ Köster, *Angew. Chem.*, **71**, 520 (1959).

³¹ Saegerbarth, *J. Am. Chem. Soc.*, **82**, 2081 (1960); *J. Org. Chem.*, **25**, 2212 (1960).

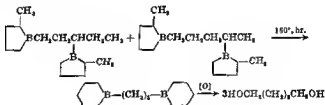
³² Brown and Zweifel, *J. Org. Chem.*, in print.

The partial hydroboration of dienes (monohydroboration) followed by oxidation gives the corresponding alcohols in modest yields²⁹ 1,5-Hexadiene is transformed into 5-hexene-1-ol, and cyclopentadiene³³ into 3-cyclopenten-1-ol. Bicycloheptadiene yields *exo*-dehydronorborneol (87% *exo* and 13% *endo*)²⁹



Isomerization

Dihydroboration of acyclic dienes with diborane followed by isomerization yields cyclic organoboranes. The preferred product appears to be the 6-membered heterocycle³¹. Hydroboration of 1,3-pentadiene yields what was considered to be a mixture of bis-1,3- and bis-1,4-(1-bora-2-methylcyclopentyl)pentane, for on oxidation it furnished a 1:9 mixture of 1,3- and 1,4-pentanediol. However, the product obtained after thermal isomerization and oxidation was essentially pure 1,5-pentandiol.³¹

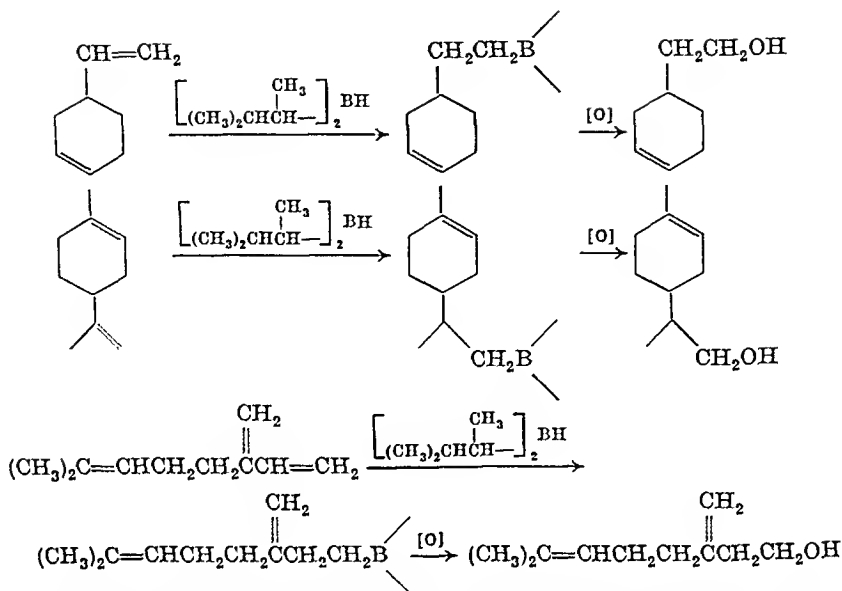


Hydroboration with Bis-(3-methyl-2-butyl)borane

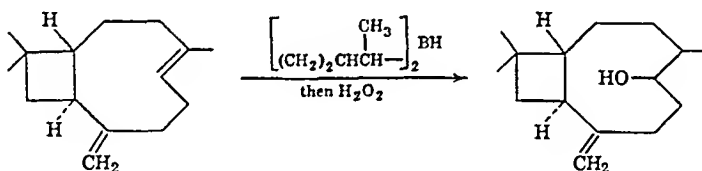
Bis-(3-methyl-2-butyl)borane has been applied to the selective hydroboration of dienes with excellent results.^{15, 34} 2-Methyl-1,5-hexadiene was converted in good yield to 5-methyl-5-hexen-1-ol, and 1,3-cyclohexadiene furnished a mixture consisting of 90% 2-cyclohexen-1-ol and 10% 3-cyclohexen-1-ol. Also, the more reactive double bonds in vinylcyclohexene, *d*-limonene, and myrcene³⁵ are hydrated without attack on the less reactive double bond(s).

²⁹ Winstein, Alfred, and Sonnenberg, *J. Am. Chem. Soc.*, **81**, 3523 (1959); Alfred, Sonnenberg, and Winstein, *J. Org. Chem.*, **25**, 28 (1960).

³¹ Zweifel, Nagase, and Brown, *J. Am. Chem. Soc.*, **84**, 180 (1962).

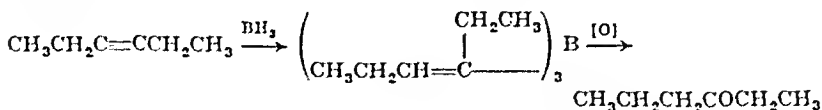


It is noteworthy that hydroboration of earyophyllene involves a preferential attack at the highly reactive *trans* internal double bond.³⁵



HYDROBORATION OF ACETYLENES

Hydroboration of disubstituted acetylenes with diborane proceeds readily and can be controlled to give predominantly the vinylorgano-borane. Oxidation of the latter with hydrogen peroxide affords the ketone.²

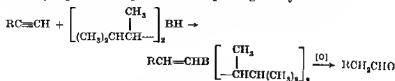


The corresponding reaction with 1-alkynes yields predominantly the dihydroboration product. However, use of either bis-(3-methyl-2-butyl)-borane or trimethylamine-*t*-butylborane³⁶ circumvents this difficulty and

³⁵ H. C. Brown and K. P. Singh, Unpublished research.

³⁶ Hawthorne, *J. Am. Chem. Soc.*, **83**, 2541 (1961).

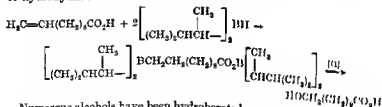
results in the formation of the monohydroborated product. Oxidation of the vinylorganoborane gives the corresponding aldehyde.



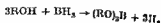
HYDROBORATION OF OLEFINS CONTAINING OTHER FUNCTIONAL GROUPS

Up to the present the hydroboration-oxidation reaction has been applied primarily to olefins, dienes, and acetylenes. Extension of the reaction to functional derivatives of such compounds is complicated by the reduction of many functional groups by diborane.^{37, 38} Fortunately, this is not an insurmountable difficulty. The hydroboration of carbon-carbon double or triple bonds is so rapid that they can frequently be converted to organoboranes in excellent yield in the presence of such functions as acid chlorides, esters, or nitro groups. In some cases a group which is reduced very rapidly, such as the carboxyl group, can be tolerated.

For example, methyl oleate has been converted to 9- and 10-hydroxystearic acid via hydroboration.³⁹ Similarly bis-(3-methyl-2-butyl)borane, which reacts with but does not reduce the carboxyl group under hydroboring conditions, has been utilized to convert 10-undecenoic acid to 11-hydroxyundecanoic acid.³⁸



Numerous alcohols have been hydroborated, especially steroidal alcohols. The presence of one or more free hydroxyl groups requires a corresponding excess of the hydroborating agent. The boric esters formed do not interfere with the hydroboration.



Finally, there are many functional groups that are relatively inert toward diborane or other hydroborating agents. Hydroboration of

³⁷ Brown and Subba Rao, *J. Am. Chem. Soc.*, **82**, 881 (1960); Brown and Korytnyk, *ibid.*, **82**, 3866 (1960).

³⁸ Brown and Bigley, *J. Am. Chem. Soc.*, **83**, 486 (1961).

³⁹ Fore and Beckford, *J. Org. Chem.*, **24**, 920 (1959).

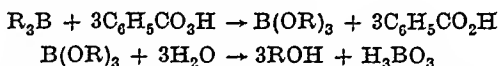
unsaturated derivatives containing these substituents appears to offer no difficulty. The following examples are illustrative.

Vinyltrimethylsilane was readily hydroborated and converted to the corresponding alcohol.¹⁴ Both *p*-chlorostyrene and *p*-methoxystyrene were converted to the corresponding alcohols; the *p*-substituents merely affected the ratio of the two isomeric alcohols produced.¹³ Ethyl vinyl ether,⁴⁰ allyl methyl sulfide,⁷ and allyl chloride⁴¹ have been hydroborated. The organoborane derived from allyl chloride yields 3-chloropropanol on oxidation.⁴¹ On treatment with base, however, it cyclizes to cyclopropane.⁴²

OXIDATION OF ORGANOBORANES

Whereas alkylboranes of low molecular weight are spontaneously flammable in air, tri-*n*-butylborane and higher homologs react with oxygen but do not inflame. Since air oxidation has not proved valuable in synthesis, it will not be discussed here.

Perbenzoic acid reacts practically quantitatively with tri-*n*-butylborane in chloroform solution. All three alkyl groups are cleaved with the formation of *n*-butyl alcohol and boric acid.⁵



Aqueous hydrogen peroxide in the presence of dilute alkali effects a complete dealkylation of tri-*n*-butylborane.⁴³ The reaction was suggested as the basis of a convenient method for the determination of boron in organoboranes⁵ and was later developed as an analytical procedure.⁴⁴ However, the vigorous conditions used involved heating the organoborane with excess hydrogen peroxide and concentrated sodium hydroxide under reflux.

Early applications of this reaction in the hydroboration-oxidation studies also utilized more vigorous conditions¹ than were subsequently found necessary. Hydrogen peroxide concentration, base concentration, and oxidation temperature can be varied widely without affecting the yield significantly.⁶ The results are summarized in Table VI.

Standard conditions for the oxidation were defined as follows: 16.6 mmoles of tri-*n*-hexylborane in 40 ml. of diglyme was treated with 15 mmoles of sodium hydroxide (5 ml. of 3*N* solution), followed by the

⁴⁰ Mikhailov and Shegoleva, *Bull. Acad. Sci. USSR., Div. Chem. Sci. (English Transl.)*, 1959, 518.

⁴¹ H. C. Brown and K. Keblys. Unpublished research.

⁴² Hawthorne and Dupont, *J. Am. Chem. Soc.*, 80, 5830 (1958); Hawthorne, *ibid.*, 82, 1886 (1960).

⁴³ Snyder, Kuck, and Johnson, *J. Am. Chem. Soc.*, 60, 105 (1938).

⁴⁴ Belcher, Gibbons, and Sykes, *Mikrochim. Acta.*, 40, 76 (1952).

TABLE VI

EFFECT OF HYDROGEN PEROXIDE CONCENTRATION, BASE CONCENTRATION, AND TEMPERATURE IN THE OXIDATION OF TRI-*n*-HEXYLBORANE


Hydrogen Peroxide Added, % of Theory	NaOH, mmoles	Temp, °C.	Yield, % of 1-hexanol
72	45	25-35	80
95	45	25-35	97
120	45	25-35	98
150	45	25-35	97
100	45	25-35	97
100	30	25-35	92
100	15	25-35	94
100	0	25-35	57
100	45	0-5	89
100	45	25-35	97
100	45	50-55	96
100	45	75-80	97

slow addition of 60 mmoles of hydrogen peroxide, 20% excess (6.0 ml of a 30% solution) The amount of 1-hexanol obtained was determined by gas-liquid partition chromatography. The oxidation was achieved equally well in tetrahydrofuran. In diethyl ether, however, reaction was more sluggish, presumably because of the immiscibility of the solvent with water. The addition of ethanol as a cosolvent circumvented this difficulty and the yield under these conditions was 98%.⁸

As indicated in Table VII, wide variations in the structure of the organoborane do not affect the oxidation greatly.

TABLE VII

EFFECT OF STRUCTURE UPON OXIDATION

Organoborane	Yield, % of alcohol
	97
$[(CH_3)_3CCH_2CH(CH_3)CH_2-]_3B$	95
$\left[\begin{array}{c} CH(CH_3)_2 \\ \\ (CH_3)_3CCH- \end{array} \right]_2 BH$	79
$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_2 BH$	98
$(C_6H_5CH_2CH_2-)_3B$	99

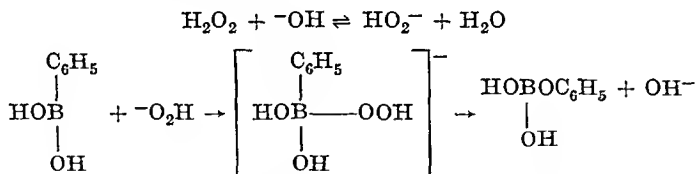
Numerous substances, such as olefins, dienes, acetylenes, esters, ketones, and nitriles, may be present without influencing the yield of alcohol or undergoing any reaction themselves. The results with such additives present are summarized in Table VIII.

TABLE VIII

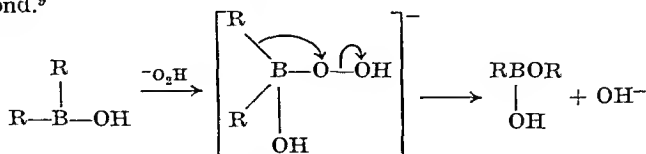
EFFECT OF ADDED SUBSTANCES (50 MMOLES) ON THE OXIDATION OF TRI-*n*-HEXYLBORANE (16.6 MMOLES)

Substance Added	Recovery of Added Substance After Oxidation, %	Yield, % of <i>n</i> -hexanol
1-Hexene	96	95
1,3-Cyclohexadiene	96	95
1-Hexyne	92	100
Isobutyraldehyde	63	97
Ethyl acetate	92	95
<i>n</i> -Butyl bromide	93	99
Acetonitrile	97	99

Although no detailed kinetic studies of the oxidation reaction of alkylboranes have been reported, Kuivila and co-workers have studied the related reaction of benzeneboronic acid with hydrogen peroxide.⁴⁵ The following mechanism was proposed.



Wechter proposed an identical mechanism for the oxidation of the alkylboron bond.⁹



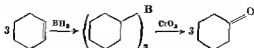
In this mechanism the group R shifts with its pair of electrons from boron to oxygen. This is consistent with the retention of configuration observed in the hydroboration-oxidation of cyclic olefins.

Organoboranes can be oxidized to ketones by chromic acid.⁴⁶ The use

⁴⁵ Kuivila, *J. Am. Chem. Soc.*, **76**, 870 (1954); **77**, 4014 (1955); Kuivila and Wiles, *ibid.*, **77**, 4830 (1955); Kuivila and Armour, *ibid.*, **79**, 5659 (1957).

⁴⁶ Pappo, *J. Am. Chem. Soc.*, **81**, 1010 (1959).

of this reagent makes it possible to go from a cyclic olefin such as cyclohexene to the corresponding ketone, cyclohexanone, in satisfactory yield without isolating the secondary alcohol.⁴⁷



EXPERIMENTAL CONDITIONS

The preparation and handling of organoboranes require techniques and precautions similar to those used for the Grignard reaction. Although the necessity for a nitrogen atmosphere has not been established, hydroboration reactions are normally carried out under nitrogen. It is convenient to transfer solutions of diborane and dialkylboranes by means of a hypodermic syringe.

Earlier reports have stressed the hazardous nature of diborane. However, during the exploration of the hydroboration reaction no difficulties have been encountered in the preparation and handling of dilute solutions of diborane and dialkylboranes. Even when solutions of diborane or dialkylboranes in tetrahydrofuran or diglyme were exposed to air, they did not inflame spontaneously but were slowly oxidized. Nevertheless, adequate ventilation is recommended.

Hydroboration With Diborane Generated *in Situ*

In this procedure an acid is added slowly in an inert atmosphere to a mixture of the unsaturated compound and the hydride in an appropriate solvent. Since no diborane is liberated, the method possesses many advantages for large-scale preparations where the presence of the hydride and the inorganic reaction product, e.g., sodium borofluoride, offers no difficulty. Therefore it is most useful when the organoborane is desired simply as an intermediate for further reaction.

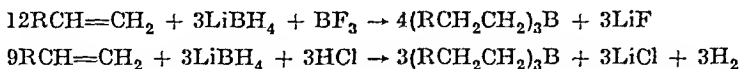
Sodium borohydride is essentially insoluble in common ether solvents, but readily soluble in diglyme (dimethyl ether of diethylene glycol) and triglyme (dimethyl ether of triethylene glycol). Consequently, these solvents are used with sodium borohydride.⁴⁸ However, numerous procedures have been developed for utilizing metal hydrides and complex hydrides in the preparation of diborane and related reactions so as to avoid the necessity for a particular solvent or reagent.⁴⁹

⁴⁷ Brown and Garg, *J. Am. Chem. Soc.*, **83**, 2951 (1961).

⁴⁸ Brown, Mead, and Subba Rao, *J. Am. Chem. Soc.*, **77**, 4878 (1955).

⁴⁹ Brown, K. J. Murray, L. J. Murray, Snover, and Zweifel, *J. Am. Chem. Soc.*, **82**, 4233 (1960).

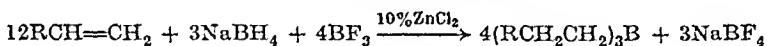
Lithium borohydride is readily soluble in diethyl ether and tetrahydrofuran as well as in other ether solvents. In diethyl ether the essentially quantitative hydroboration of 1-octene was achieved with boron trifluoride etherate, hydrogen chloride, and sulfuric acid. Lithium borohydride requires only sufficient boron trifluoride to convert the lithium to lithium fluoride.



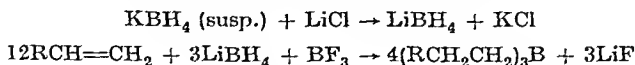
Sodium borohydride is soluble in diglyme and triglyme, and the hydroboration reactions with boron trifluoride etherate, hydrogen chloride, or sulfuric acid proceed rapidly and quantitatively at room temperature.

Although the solubility of sodium borohydride in tetrahydrofuran is small, the hydroboration of an olefin is readily achieved by treating with boron trifluoride a suspension of sodium borohydride in tetrahydrofuran containing the olefin.^{49,50} Alternatively, a solution of diborane in tetrahydrofuran can be prepared by treating a suspension of sodium borohydride in that solvent at 0° with hydrogen chloride. Hydroboration is then accomplished by adding the olefin to this solution.

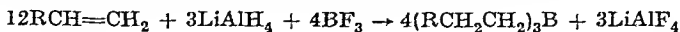
Finally, it is possible to utilize diethyl ether as the solvent by introducing 10 mole % of anhydrous zinc chloride to catalyze the reaction between sodium borohydride and boron trifluoride etherate.



Potassium borohydride, although only slightly soluble in triglyme and in tetrahydrofuran, can be utilized as a suspension in these solvents. A potassium borohydride suspension in triglyme will react directly with boron trifluoride etherate, while a suspension in tetrahydrofuran will react with lithium chloride to form the soluble lithium borohydride.⁵¹ The latter can be utilized for the hydroboration.⁴⁹



Lithium aluminum hydride with boron trifluoride etherate appears to be a convenient reagent for hydroboration in diethyl ether.^{52,53}



⁵⁰ Schubert and Lang, *Angew. Chem.*, **72**, 994 (1960).

⁵¹ Paul and Joseph, *Bull. Soc. Chim. France*, **1952**, 550.

⁵² Wolfe, Nussim, Mazur, and Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

⁵³ Sondheimer and Wolfe, *Can. J. Chem.*, **37**, 1870 (1959).

TABLE IX
CONVENIENT PROCEDURES FOR HYDROBORATION WITH
VARIOUS HYDRIDE REAGENTS⁴⁹

Solvent	Hydride Source	Acid	Molar Ratio Hydride : Acid : Olefin			1-Octene, % reacted in 1 hr. at 25°
Diglyme	NaBH ₄	BF ₃	3	4	12	99
		BCl ₃	3	4	12	98
		AlCl ₃	3	1	9	50
		HCl	2	2	6	94
		H ₂ SO ₄	2	1	6	91
		CH ₃ I	2	2	6	95
THF ^a	NaBH ₄	BF ₃	3	4	12	99
Diethyl ether	NaBH ₄ /ZnCl ₂	BF ₃	3	4	12	94
THF	KBH ₄ /LiCl	BF ₃	3	1	12	83
Diglyme	LiBH ₄	BF ₃	3	4	12	98
		BCl ₃	3	1	12	92
THF	LiBH ₄	BF ₃	3	1	12	99
		HCl	2	2	6	95
		H ₂ SO ₄	2	1	6	99
		BF ₃	3	1	12	87
Diethyl ether	LiBH ₄					
		HCl	2	2	6	95
		H ₂ SO ₄	2	1	6	92
		BF ₃	3	4	12	80 ^b
		BCl ₃	3	4	12	95
Diglyme	NaH	BF ₃	6	8	6	99
THF	NaH	BF ₃	6	8	6	99
Diglyme	LiH	BF ₃	6	8	6	95
THF	LiH	BF ₃	6	8	6	95
Diethyl ether	LiH	BF ₃	6	8	6	93
Benzene	C ₂ H ₅ N·BH ₃	BF ₃	1	1	3	90 ^c

^a THF is tetrahydrofuran.

^b Cyclohexene was the olefin in this experiment ⁴³

^c This experiment was run for 16 hours at 75°.

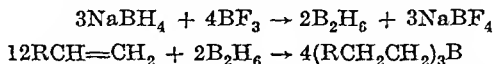
The most convenient hydroboration procedures are summarized in Table IX. It is to be noted that lithium borohydride in tetrahydrofuran or in diethyl ether requires less boron trifluoride than does sodium borohydride or lithium aluminum hydride.

Hydroboration With Diborane Generated Externally

Hydroboration with diborane produces the organoborane in essentially quantitative yield and free of inorganic salt or other by-products. In this

procedure, diborane, prepared by the addition of sodium borohydride in diglyme to boron trifluoride etherate, is passed into a solution of the olefin in an ether solvent. Tetrahydrofuran has two distinct advantages as a reaction medium: it is an excellent solvent for diborane, and it is readily distilled from the reaction products.

Sodium borohydride in diglyme absorbs a half-molar equivalent of diborane, forming sodium diborohydride ($\text{NaBH}_4 \cdot \text{BH}_3$ or NaB_2H_7).⁵⁴ Because of the formation of this species, the addition of boron trifluoride etherate to a diglyme solution of sodium borohydride does not liberate diborane until nearly half of the acid has been added. Consequently, to generate diborane smoothly it is preferable to add the solution of sodium borohydride to an excess of boron trifluoride in diglyme.



Alternatively, a 1*M* solution of diborane in tetrahydrofuran may be prepared and then utilized for the hydroboration. Such solutions can be kept at 0–5° for several weeks without significant change in the diborane concentration.

Solvents

In order to avoid losses of active hydride in the hydroboration stage, it is important that the solvents be free of water and peroxides.

Diglyme (dimethyl ether of diethylene glycol, b.p. 162°) (Ansul Chemical Co.) is purified in the following way: 1 l. of diglyme is stored over 10 g. of small pieces of calcium hydride for 12 hours. The diglyme is then decanted into a distilling flask and sufficient lithium aluminum hydride is added to ensure an excess of active hydride. The solvent is distilled at 62–63°/15 mm.

Triglyme (dimethyl ether of triethylene glycol, b.p. 212°) is purified as described for diglyme. The solvent is distilled at 107–108°/15 mm.

Tetrahydrofuran (pure grade) is treated with lithium aluminum hydride as just described, then distilled at atmospheric pressure; b.p. 66–67°.

Diethyl ether (anhydrous reagent grade) is utilized without purification.

In order to inhibit peroxidation during storage of these solvents, it is advantageous to add 0.01 % of sodium borohydride.

Boron Trifluoride Etherate

Boron trifluoride diethyl etherate, 500 ml., is treated with 10 ml. of anhydrous diethyl ether (to ensure an excess of this component) and

⁵⁴ Brown and Tierney, *J. Am. Chem. Soc.*, **80**, 1552 (1958).

distilled in an all glass apparatus at 46°/10 mm. from 2 g. of granular calcium hydride. The hydride removes small quantities of volatile acids and greatly reduces bumping during the distillation. The density of the product at 25° is 1.125.

Metal Hydrides

Sodium borohydride (98%) from Metal Hydrides, Inc., may be used without purification. Commercial lithium borohydride and potassium borohydride were used without purification after analysis for active hydrogen.

EXPERIMENTAL PROCEDURES

Procedures in Which Diborane Is Generated *in Situ*

The apparatus consists of a three-necked flask equipped with a condenser fitted with a calcium chloride tube, a pressure-equalizing dropping funnel, a thermometer, and a stirrer (a magnetic stirrer may be utilized for small-scale experiments). The apparatus is dried in an oven and assembled under dry nitrogen. Alternatively, it can be flamed dry in a stream of dry nitrogen.

To the flask are added the olefin and the hydride in an appropriate solvent. A 10–20% excess of the hydride is generally used. A quantity of acid, equivalent to the hydride used and generally in a solvent, is added dropwise in a nitrogen atmosphere. After completion of the addition, the excess hydride is carefully decomposed by water or ethylene glycol. The organoborane obtained can be oxidized *in situ* with alkaline hydrogen peroxide.

Isopinocampheol from α -Pinene (Use of Sodium Borohydride and Boron Trifluoride Etherate in Diglyme).^{11, 45} In a 300-ml. flask are placed 82.5 ml. of a 1M solution of sodium borohydride in diglyme



(10% excess) and 27.2 g. of α -pinene (0.20 mole; n_D^{20} 1.4648, $[\alpha]_D^{20}$ +46.8°) in 20 ml. of diglyme. The flask is immersed in a water bath ($\sim 20^\circ$). From the dropping funnel 14 ml. of boron trifluoride etherate (15.62 g., 0.11 mole) is added dropwise to the stirred reaction mixture over a period

⁴⁵ H. C. Brown, K. P. Singh, and G. Zweifel. Unpublished research.

of 30 minutes, while the temperature is maintained at 20–25°. The flask is kept for 1 hour at this temperature. Excess hydride is then decomposed by the careful dropwise addition of 20 ml. of water.

The organoborane (R_2BH) is oxidized at 30–50° by the immediate addition of 22 ml. of 3*N* sodium hydroxide, followed by the dropwise addition of 22 ml. of 30% hydrogen peroxide. The reaction mixture is left for 1 hour at room temperature and is then extracted with 150 ml. of ether. The ethereal extract is washed five times with equal amounts of ice water to remove diglyme, and dried over anhydrous magnesium sulfate. The product obtained after removal of the solvent is crystallized from a small amount of petroleum ether (35–37°). There is obtained 24.3 g. (79%) of isopinocampheol: m.p. 55–57°, $[\alpha]_D^{20}$ –32.8° (c, 1% in benzene).

4-Methyl-1-pentanol from 4-Methyl-1-pentene (Use of Sodium Borohydride and Boron Trifluoride Etherate in Tetrahydrofuran).⁴⁹ To a well-stirred suspension of 3.4 g. (90 mmoles) of pulverized sodium borohydride in 150 ml. of tetrahydrofuran containing 25.2 g. of 4-methyl-1-pentene (0.30 mole; n_D^{20} 1.3830) is added 15.1 ml. of boron trifluoride etherate (17.0 g., 0.120 mole) in 20 ml. of tetrahydrofuran over a period of 1 hour, while the temperature is maintained at 25°. The flask is kept an additional hour at 25° before the excess hydride is decomposed with water.

The organoborane is oxidized at 30–40° (water bath) by the addition of 32 ml. of a 3*N* solution of sodium hydroxide, followed by the dropwise addition of 32 ml. of 30% hydrogen peroxide. The reaction mixture is saturated with sodium chloride. The tetrahydrofuran layer formed is separated, and then washed with saturated aqueous sodium chloride. The extract is dried over anhydrous magnesium sulfate.

Distillation furnished, after removal of the tetrahydrofuran, 24.5 g. (80%) of 4-methyl-1-pentanol, b.p. 151–153°/735 mm; n_D^{20} 1.4140.

2,4,4-Trimethyl-1-pentanol from 2,4,4-Trimethyl-1-pentene (Use of Lithium Borohydride and Sulfuric Acid in Tetrahydrofuran).⁴⁹ In a 500-ml. flask are placed 2.62 g. of lithium borohydride (0.12 mole), 33.6 g. of 2,4,4-trimethyl-1-pentene (0.30 mole, n_D^{20} 1.4807), and 170 ml. of tetrahydrofuran. Concentrated sulfuric acid (5.88 g., 60 mmoles) in 42 ml. of diethyl ether is added over a period of 1 hour to the lithium borohydride-olefin solution, the temperature being maintained at 25°. The reaction is permitted to proceed for an additional hour at room temperature, and then the excess hydride is decomposed with water.

The organoborane is oxidized at 20–40° (water bath) by the addition of 32 ml. of a 3*N* solution of sodium hydroxide, followed by the dropwise addition of 32 ml. of 30% hydrogen peroxide. The tetrahydrofuran-ether layer is separated, washed with water, and dried over anhydrous magnesium sulfate.

The product obtained after removal of the solvent furnishes on distillation 31.6 g (81%) of 2,4,4-trimethyl-1-pentanol, b p 165–166°/748 mm, n_D^{20} 1.4274.

Cyclohexanol from Cyclohexene (Use of Lithium Aluminum Hydride and Boron Trifluoride Etherate in Diethyl Ether).⁵³ In a flask are placed 3.4 g. of boron trifluoride etherate (24 mmoles), 4 g. of cyclohexene (49 mmoles), and 100 ml of diethyl ether. A solution of 0.7 g. (18 mmoles) of lithium aluminum hydride in 70 ml of ether is added to the olefin-boron trifluoride mixture during 20 minutes. The mixture is stirred at room temperature for 2 hours, and then the excess hydride is decomposed by slowly adding 20 ml. of acetone. A saturated solution of sodium sulfate is added, followed by solid sodium sulfate. The mixture is filtered, and the clear filtrate evaporated.

The residue is dissolved in 30 ml of 90% ethanol containing 0.8 g. of sodium hydroxide, and 10.2 ml of 20% hydrogen peroxide is added with stirring during 5 minutes. The temperature of the reaction mixture rises to about 70°. It is maintained at this temperature for 5 minutes longer by external heating, and the flask is then cooled. Water and ether are added, and the ether extract is washed with water, dried, and evaporated. On distillation there is obtained 4.0 g (82%) of cyclohexanol, b p. 161–162°, n_D^{20} 1.4656.

Procedures in Which Diborane Is Generated Externally (Fig. 1)

exo-Norborneol from Norbornene.^{11,46} A dry 500 ml three-necked flask is equipped with a thermometer, a condenser connected to a mercury bubbler containing acetone (T-tube dipping in mercury), and a sintered glass dispersion tube. A tube from the condenser outlet dips below the surface of some mercury in a side arm test tube. Above the mercury is a layer of acetone which serves to destroy escaping diborane by reacting with it to form diisopropoxyborane, $[(CH_3)_2CHO]_2BH$.

A solution of 28.2 g (0.30 mole) of norbornene, m p 45°, in 100 ml of tetrahydrofuran is placed in the flask. The dispersion tube (completely immersed in the tetrahydrofuran olefin solution) is connected with Tygon tubing to a 300-ml two-(or three-)necked flask serving as the diborane generator.

The generator is equipped with a pressure equalizing dropping funnel (serving alternatively as an inlet for nitrogen) containing 90 ml of a 1M solution of sodium borohydride in diglyme (3.4 g, 20% excess). In the generator is placed 23 ml of boron trifluoride etherate (25.5 g, 0.18 mole, 50% excess) in 20 ml of diglyme.

⁴⁶ H. C. Brown, S. Nishida, and G. Zweifel. Unpublished research.

Diborane is generated by the dropwise addition of the sodium borohydride solution to the stirred boron trifluoride etherate-diglyme solution. The gas is passed into the olefin-tetrahydrofuran solution (maintained at 20°) by applying a slight flow of dry nitrogen through the generator.

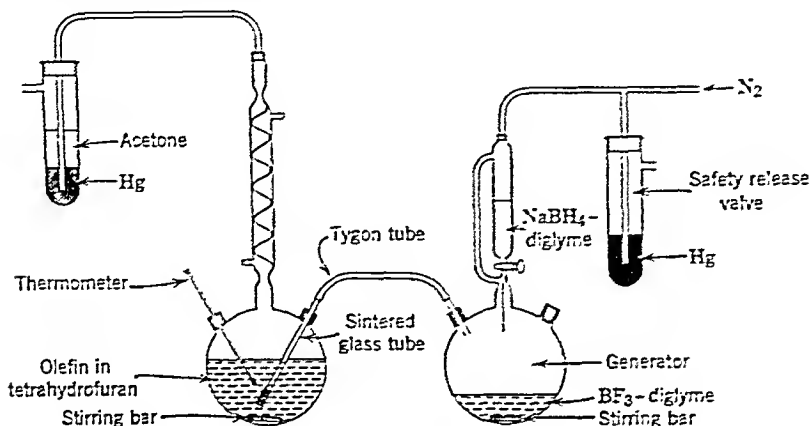


FIG. 1.

After completion of the sodium borohydride addition (1 hour), the generator is heated for 1 hour at 70–80°, the nitrogen flow being maintained to ensure the complete transfer of the diborane to the hydroboration flask. The generator is allowed to cool to room temperature and is then disconnected from the hydroboration flask.

The excess hydride in the hydroboration flask is decomposed by the careful addition of 20 ml. of water. The organoborane is oxidized at 30–50° (water bath) by the addition of 32 ml. of 3*N* sodium hydroxide, followed by dropwise addition of 32 ml. of 30% hydrogen peroxide. During the oxidation, efficient stirring is maintained. The reaction mixture is stirred for an additional hour, then 100 ml. of diethyl ether is added. The organic phase is separated, the aqueous phase is saturated with sodium chloride and then extracted twice with 50-ml. portions of ether. The combined extracts are washed twice with 50-ml. portions of saturated sodium chloride solution and dried over anhydrous magnesium sulfate.

The product obtained after removal of the solvent is crystallized from a small amount of petroleum ether to furnish 24.4 g. (74%) of *exo*-norborneol, m.p. 126–127° after sublimation.

2,3-Dimethyl-1,4-butanediol from 2,3-Dimethylbutadiene (Preparation and Use of a Solution of Diborane in Tetrahydrofuran).²⁹

A. Preparation of a Solution of Diborane in Tetrahydrofuran. The

experimental conditions and the apparatus utilized are described on p. 32

In a 1-l flask with a side arm capped by a rubber septum to permit the removal of material is placed 500 ml of tetrahydrofuran. The flask is immersed in an ice bath. Diborane, generated by the addition of 950 ml. of a 1M solution of sodium borohydride in diglyme to 1.90 moles of boron trifluoride etherate (50% excess), is passed through a solution of sodium borohydride (to remove traces of boron trifluoride) into the tetrahydrofuran.

Determination of the boron by titration and hydride by hydrolysis shows that the solution is ~ 1 M in diborane. The concentration of the diborane does not change significantly over a period of several weeks when the solution is kept under nitrogen at 0°.

B Hydroboration-Oxidation In a 300-ml. flask is placed 8.2 g. (0.10 mole) of 2,3-dimethyl-1,3-butadiene in 100 ml of tetrahydrofuran. The flask is immersed in an ice bath. Fifty milliliters of a 1M solution of diborane in tetrahydrofuran is added slowly to the diene-tetrahydrofuran solution. After the addition the flask is kept for 30 minutes at room temperature, and the excess hydride is decomposed by the careful addition of water.

The organoborane is oxidized at 30–50° (water bath) by the addition of 24 ml. of 3N sodium hydroxide, followed by the dropwise addition of 24 ml of 30% hydrogen peroxide. After 1 hour at room temperature, 75 g of potassium carbonate is added with moderate stirring. The tetrahydrofuran layer is separated, and the aqueous phase extracted twice with 30-ml portions of tetrahydrofuran. The extracts are combined and dried over anhydrous magnesium sulfate.

The solvent is removed and the product is distilled. The yield of 2,3-dimethyl-1,4-butanediol (b.p. 105–106°/2 mm, n_D^{20} 1.4563) is 7.8 g (66%).

n-Octanal from 1-Octyne [Preparation and Use of Bis-(3-methyl-2-butyl)borane].² *A.* In a three-necked flask are placed 33.6 g of 2-methyl-2-butene (0.48 mole) and 180 ml of a 1M solution of sodium borohydride in diglyme. The flask is immersed in an ice bath. Boron trifluoride etherate, 0.24 mole, is added dropwise to the reaction mixture, efficient stirring being maintained. The flask is permitted to remain for 2 hours at 0° and is then placed in an ice-salt bath.

B To the reagent (0.24 mole) prepared in *A*, 22.0 g. (0.20 mole) of 1-octyne in 20 ml of diglyme is added as rapidly as possible while the temperature is maintained at 0–10°. The reaction mixture is permitted to warm to room temperature to complete the hydroboration.

The organoborane is oxidized at 0° by the addition of 150 ml. of a 15%

solution of hydrogen peroxide, while the *pH* of the reaction mixture is maintained at 7–8 by the controlled addition of 3*N* sodium hydroxide. The reaction mixture is then neutralized and steam distilled. The distillate is extracted with ether and the extract dried over anhydrous magnesium sulfate. Distillation yields 18.0 g. (70%) of *n*-octanal, b.p. 83–85°/33 mm., n_D^{20} 1.4217.

(+)-2-Butanol from *cis*-2-Butene (Preparation of Diisopinocampheylborane and Use in Asymmetric Synthesis).^{17,57} *A.* In a 500-ml. flask fitted with a condenser, a pressure-equalizing dropping funnel, and a thermometer are placed 75 ml. of 1*M* sodium borohydride (2.85 g.) in diglyme and 27.2 g. (0.2 mole) of (–)- α -pinene, $[\alpha]_D^{20}$ –47.8° in 100 ml. of diglyme. The flask is immersed in an ice bath and 12.6 ml. (14.2 g., 0.10 mole) of boron trifluoride etherate is added dropwise to the well-stirred reaction mixture. Stirring is continued for 4 hours at 0–5°. The diisopinocampheylborane separates as a thick white precipitate.

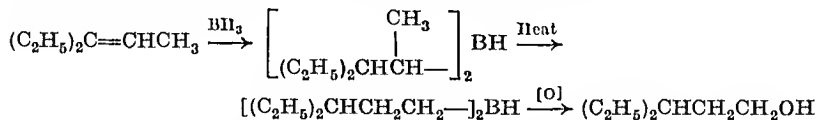
B. cis-2-Butene (8.5 ml., 6.1 g., 0.11 mole) is condensed at –78° and then introduced to the well-stirred diisopinocampheylborane. The reaction flask is equipped with a cold trap in order to minimize the loss of *cis*-2-butene. The reaction mixture is stirred for 2 hours at 0–5°, then allowed to warm to room temperature (2 hours). The excess hydride is decomposed by the addition of 10 ml. of water.

The organoborane is oxidized at 30–50° (water bath) by the addition of 32 ml. of 3*N* sodium hydroxide and 32 ml. of 30% hydrogen peroxide. The temperature is maintained at 45° for an additional hour.

The reaction mixture is extracted with three 100-ml. portions of ether. The combined extracts are washed with saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. The ether is removed and the product distilled. There is obtained 6.15 g. (83%) of 2-butanol; b.p. 98°/725 mm., n_D^{20} 1.3970 $[\alpha]_D^{20}$ +11.6°.

The isopinocampheol formed in this reaction is obtained in 92% yield by distillation.

3-Ethyl-1-pentanol from 3-Ethyl-2-pentene (Preparation and Isomerization of an Alkylborane).⁵⁸ *A.* To 50 ml. of diglyme



cooled in an ice bath is added 25 ml. of boron trifluoride etherate. The ether is removed by applying a vacuum of 5–10 mm. for 20 minutes while the flask is kept at 20–25°. The resulting boron trifluoride diglymate is

⁵⁷ H. C. Brown, N. R. Ayyangar, and G. Zweifel. Unpublished research.

⁵⁸ H. C. Brown and G. Zweifel. Unpublished research.

TABLE X
HYDROBORATION-OXIDATION OF OLEFINS

No. of C Atoms	Olefin	Hydroborating Agent	Oxidation Product(s)	Isomer Distribu- tion, %	Yield, %	References
C ₄	Olefin	NaBH ₄ -BF ₃ -Diglymo	1-Butanol	93	90-95*	13
	1-Butene	NaBH ₄ -BF ₃ -Diglymo	2-Butanol	7		
			1-Pentanol	94	90-95*	1, 13
	1-Pentene	NaBH ₄ -BF ₃ -Diglymo	2-Pentanol	6		
			2-Pentanol	51-55	90-95*	13
C ₅	2-Pentene (<i>cis</i> or <i>trans</i>)	NaBH ₄ -BF ₃ -Diglymo	3-Pentanol	45-49		
			2-Pentanol	99	90-95*	13
	2-Methyl-1-butene	NaBH ₄ -BF ₃ -Diglymo	2-Methyl-1-butanol	1		
			2-Methyl-2-butanol	98	98*	6, 13
	2-Methyl-2-butenone	NaBH ₄ -BF ₃ -Diglymo	3-Methyl-2-butanol	2		
C ₆	3-Methyl-1-butenone	NaBH ₄ -BF ₃ -Diglymo	3-Methyl-1-butanol	94	90-95*	13
			3-Methyl-2-butanol	6		
	Cyclopentene	NaBH ₄ -AlCl ₃ -Diglymo	Cyclopentanol		80	4
		B ₂ H ₆ -Triglymo	Cyclopentanol		90	1
		NaBH ₄ -AlCl ₃ -Diglymo	1-Hexanol		90	4
C ₆	1-Hexene	B ₂ H ₆ -Diglymo	1-Hexanol		87	1
		NaBH ₄ -BF ₃ -Diglymo	1-Hexanol	94	95	1, 13
			2-Hexanol	6		
			1-Hexanol	99	85-90*	15
			2-Hexanol	1		
C ₆	2-Hexene (<i>cis</i> and <i>trans</i>)	B ₂ H ₆ -Diglymo	2- and 3-Hexanol		80	1
		NaBH ₄ -BF ₃ -Diglymo	2-Hexanol	46-50	90	1, 13
			3-Hexanol	50-54		
			3-Hexanol	100	90-95*	13
			3,3-Dimethyl-1-butanol		67	4
C ₆	<i>cis</i> -3-Hexeno	NaBH ₄ -BF ₃ -Diglymo	3,3-Dimethyl-1-butanol		62	1
	3,3-Dimethyl-1-butenone	NaBH ₄ -AlCl ₃ -Diglymo	3,3-Dimethyl-1-butanol			
		B ₂ H ₆ -Triglymo	3,3-Dimethyl-1-butanol	94		1, 13
		NaBH ₄ -BF ₃ -Diglymo	3,3-Dimethyl-2-butanol	6		









C ₁	4 Methyl 1-pentene	NaBH ₄ -BF ₃ -THF			
	<i>trans</i> -4-Methyl-2-pentene	NaBH ₄ -BF ₃ -Diglyme			
		$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \\ \\ \text{BH} \end{array} \right]_3$			
	<i>cis</i> 4 Methyl-2-pentene	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \\ \\ \text{BH} \end{array} \right]_3$			
	Cyclohexene	LiAlH ₄ -BF ₃ -diethyl ether			
	1-Methylcyclopentene	B ₂ H ₆ -THF			
	4,4 Dimethyl-1-pentene	NaBH ₄ -BF ₃ -Diglyme			
	<i>trans</i> 4,4-Dimethyl 2-pentene	NaBH ₄ -BF ₃ -Diglyme			
	3 Ethyl-1-pentene	NaBH ₄ -BF ₃ -Diglyme			
	3 Ethyl 2 pentene	NaBH ₄ -BF ₃ -Diglyme			
C ₄	1 Methylcyclohexene	B ₂ H ₆ -THF			
	3 Methylcyclohexene	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \\ \\ \text{BH} \end{array} \right]_3$			
	1,2 Dimethylcyclopentene	B ₂ H ₆ -THF			
	Norbornene	B ₂ H ₆ -THF			
	1-Octene	LiBH ₄ -BF ₃ -diethyl ether			
	2,4,4 Trimethyl-1-pentene	LiAlH ₄ -BF ₃ -diethyl ether			
		NaBH ₄ -HCl-THF			
		LiBH ₄ -H ₂ SO ₄ -THF			
		NaBH ₄ -BF ₃ -Diglyme			
	2,4,4 Trimethyl-2-pentene	NaBH ₄ -BF ₃ -Diglyme			
	4-Methyl 1 pentanol		57	80	49
	4 Methyl 2 pentanol		43		13
	2 Methyl 3-pentanol				
	4-Methyl 2 pentanol		95	85-90*	15
	2 Methyl 3 pentanol		5		
	4-Methyl-2 pentanol		97	85-90*	15
	2 Methyl 3-pentanol		3		
	Cyclohexanol			80	53
	<i>trans</i> 2 Methylcyclopentanol			86	11
	4,4 Dimethyl 1 pentanol		93	85-90*	13
	4,4-Dimethyl-2-pentanol		7		
	4,4 Dimethyl-2 pentanol		58		13
	2,2-Dimethyl 3-pentanol		42		
	3-Ethyl 1-pentanol		90	85	23
	3 Ethyl-2-pentanol		10		
	3 Ethyl 2 pentanol			83	23
	<i>trans</i> 2 Methylcyclohexanol			85	11
	2 Methylcyclohexanol		48	—	11
	(<i>cis</i> and <i>trans</i>)				
	3-Methylcyclohexanol		52		
	(<i>cis</i> and <i>trans</i>)				
	<i>cis</i> -1,2 Dimethylcyclopentanol			80	11
	<i>cis</i> Norborneol		99	75-85	11
	<i>cis</i> Norborneol			70	49
	1 Octanol			80	53
	1-Octanol			80	49
	2,4,4 Trimethyl-1 pentanol		99	81	49
	2,4,4-Trimethyl 1 pentanol		1	—	13
	2,4,4-Trimethyl 2-pentanol		2		
	2,4,4 Trimethyl-2-pentanol		98	79*	6,13
	2,4,4 Trimethyl-3 pentanol				

Note. References 59 to 70 are on p 54.

* The yield was determined by vapor phase chromatography.

TABLE X—Continued
HYDROBORATION-OXIDATION OF OLEFINS

No. of C Atoms	Olefin	Hydroborating Agent	Oxidation Product(s)	Isomer Distribu- tion, %	Yield, %	References
C ₆ (cont'd.)	Olefin	B ₃ H ₆ ·THF	<i>cis</i> -1,2-Dimethylcyclo- hexanol	—	82	11
	1,2-Dimethylcyclo- hexene	B ₃ H ₆ ·THF	2,2-Dimethylcyclohexanol	50	—	11
	3,3-Dimethylcyclo- hexene	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_2\text{CHCH} \end{array} \right]_3 \text{BH}$	3,3-Dimethylcyclohexanol	50	—	11
			2,2-Dimethylcyclohexanol	40	—	11
C ₉	Styrene	NaBH ₄ ·AlCl ₃ -Diglyme LiBH ₄ ·BF ₃ -diethyl ether	2-Phenyl-1-ethanol	20	81	4
		B ₃ H ₆ -Diglyme	1-Phenyl-1-ethanol	80	94*	13
		NaBH ₄ ·BF ₃ -Diglyme	2-Phenyl-1-ethanol	18	95*	13
		NaBH ₄ ·BF ₃ -Diglyme	1-Phenyl-1-ethanol	82	94*	13
C ₉	α -Methylstyrene	NaBH ₄ ·BF ₃ -Diglyme	2-Phenyl-1-ethanol	20	—	1, 13
	<i>p</i> -Methylstyrene	NaBH ₄ ·BF ₃ -Diglyme	2-Phenyl-1-ethanol	80	—	13
	Allylbenzene	NaBH ₄ ·BF ₃ -Diglyme	2-Phenyl-1-propanol	100	92	13
			1- <i>p</i> -Tolyl-1-ethanol	18	—	13
C ₁₀	<i>trans</i> -1-Phenylpropene	NaBH ₄ ·BF ₃ -Diglyme	1-Phenyl-2-propanol	10	—	13
	1-Decene	NaBH ₄ ·BF ₃ -Diglyme	1-Phenyl-1-propanol	90	—	13
	1,1-Di- <i>t</i> -butylethylene	B ₃ H ₆ -Diglyme	1-Phenyl-2-propanol	85	—	13
	1,2-Di- <i>t</i> -butylethylene	B ₃ H ₆ -Diglyme	1-Phenyl-2-propanol	15	—	13
C ₁₀	1-Phenylcyclobutene	B ₃ H ₆ ·THF	1-Decanol	85	85	1
			[(CH ₃) ₂ CHCH ₂ CH ₂ OH	92	92	1
			(CH ₃) ₂ CHCH ₂ CH ₂ C(CH ₃) ₂	—	—	60
			2-Phenylcyclobutanol	—	82	12
				—	82	59

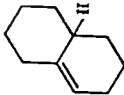
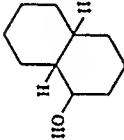
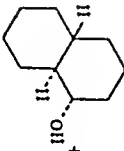
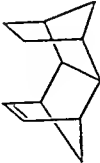
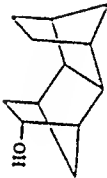
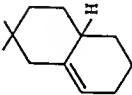
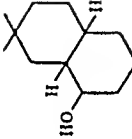
	NaBH_4 , BF_3 , Diglyme		81	11
	B_2H_6 , THF		89	11
	B_2H_6 -THF-diethyl ether		77	61
	B_2H_6 , Diglyme		28	63




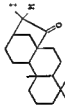
Note: References 59 to 70 are on p. 54.

* The yield was determined by vapor-phase chromatography.

† The conditions for hydroboration were not reported.

TABLE X—Continued
HYDROBORATION-OXIDATION OF OLEFINS

No. of C Atoms	Olefin	Hydroborating Agent	Oxidation Product(s)	Isomer Distribu- tion, %	Yield, % ^a	References
C ₁₁		LiAlH ₄ ·BF ₃ ·diethyl ether	 + 	—	—	53
C ₁₂		B ₃ H ₆ †		—	—	20
C ₁₂		LiAlH ₄ ·BF ₃ ·diethyl ether		—	—	53

C_{14}	1,1 Diphenylethylene	$NaBH_4, AlCl_3$, Diglyme	2,2 Diphenylethanol	71	4
					
		$NaBH_4, BF_3$, Diglyme		35	63
C_{12}		$LiAlH_4, BF_3$, diethyl ether		—	64

Note: References 59 to 70 are on p 54.

† The conditions for hydroboration were not reported

‡ The alcohol was oxidized directly to the ketone.

TABLE XI

HYDROBORATION-OXIDATION OF STEROIDS

Name	Hydroborating Agent	Oxidation Product(s)	Yield, %	Reference
Cholesterol	$B_2H_6^*$	Cholestane-3 β ,6 α -diol	45	9
		Coprostane-3 β ,6 β -diol		
	$LiAlH_4 \cdot BF_3$ -diethyl ether	Cholestane-3 β ,6 α -diol diacetate	70	52
1-Cholestene		Coprostane-3 β ,6 β -diol diacetate	10-20	
	$LiAlH_4 \cdot BF_3$ -diethyl ether	Cholestan-1 α -ol	35	16
		Cholestan-2 α -ol	40	
	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_2 BH$	Cholestan-2 α -ol	75	16
2-Cholestene		Cholestan-2 α -ol	35	16
	$LiAlH_4 \cdot BF_3$ -diethyl ether or B_2H_6 -THF	Cholestan-3 α -ol	45	
		Cholestan-2 α -ol	35	16
	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_2 BH$	Cholestan-3 α -ol	45	
3-Cholestene	$LiAlH_4 \cdot BF_3$ -diethyl ether	Cholestan-3 α -ol	40	16
		Cholestan-4 α -ol	45	
		Cholestan-3 α -ol	45	16
	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_2 BH$	Cholestan-4 α -ol	35	



TABLE XII
ASYMMETRIC SYNTHESIS OF ALCOHOLS

	Hydroborating Agent	Optically Active Alcohol (Rotation, $[\alpha]_D^{20}$)	Optical Purity, %	Yield, %	References
Olefin					
<i>cis</i> -2-Butene	Diisopinocampheylborane from (+)- α -pinene	2-Butanol (-11.8°)	87	90	17, 18
	Diisopinocampheylborane from (-)- α -pinene	2-Butanol ($+11.6^\circ$)	86	83	18
<i>cis</i> -3-Hexene	Diisopinocampheylborane from (+)- α -pinene	3-Hexanol (-6.5°)	91	81	17
<i>cis</i> -4-Methyl-2-pentene	Diisopinocampheylborane from (-)- α -pinene	4-Methyl-2-pentanol ($+16.0^\circ$)	76	—	18
	Diisopinocampheylborane from (+)- α -pinene	<i>cis</i> -Norbornool (-2.0°)	70	62	17, 18
Norbornene	Diisopinocampheylborane from (-)- α -pinene	<i>cis</i> -Norbornool ($+1.95^\circ$)	70	56	18

Note: References 59 to 70 are on p. 54.

TABLE XIII

HYDROBORATION-OXIDATION OF OLEFINS CONTAINING OTHER FUNCTIONAL GROUPS

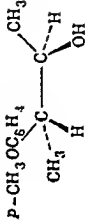
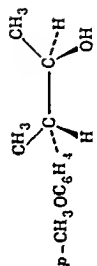
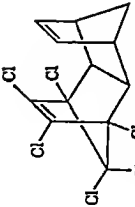
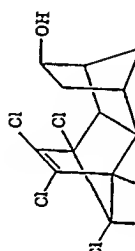
Olefin	Hydroborating Agent	Oxidation Product(s)	Isomer Distribution, %	Yield, %	References
$H_2C=CHCH_2Cl$	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_n$ BH-THP	$HOCH_2CH_2CH_2Cl$		77*	66
$H_2C=CHCH_2CH_2Cl$	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_n$ BH-THP	$HOCH_2CH_2CH_2CH_2Cl$		85*	66
$(CH_3)_3SiCH=CH_2$	$NsBH_2$, $AlCl_3$, Diglyme	$(CH_3)_3SiCH_2CH_2OH$ $(CH_3)_3SiCH(OH)CH_3$	63 37	75	14
	B_2H_6 , THF			63	67
$H_2C=CHCH_2CO_2C_2H_5$	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_n$ BH-THP	$HOCH_2CH_2CH_2CO_2C_2H_5$		76	66
$H_2C=CHCH_2CH_2CO_2C_2H_5$	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_n$ BH-THP	$HOCH_2CH_2CH_2CH_2CO_2C_2H_5$		78	66
<i>p</i> Chlorostyrene	$NaBH_4$, BF_3 , Diglyme	1 <i>p</i> Chlorophenyl 2 ethanol 1 <i>p</i> Chlorophenyl 1 ethanol	65 35	—	13
<i>p</i> Methoxystyrene	$NaBH_4$, BF_3 , Diglyme	1 <i>p</i> -Anisyl 2 ethanol 1 <i>p</i> -Anisyl 1 ethanol	91 9	—	13
1,2 O Isopropylidene-4 vinyl α D xylofuranose	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_n$ B_2H_6 †	1 <i>p</i> -Anisyl 2 ethanol 1 <i>p</i> -Anisyl 1 ethanol	98 2	80	15
		5 Deoxy 1,2 O isopropylidene- α D xylohexofuranose		—	68

Note: References 59 to 70 are on p. 54.

* The yield was determined by vapor phase chromatography.

† The conditions for hydroboration were not reported.

TABLE XIII—Continued

Olefin	Hydroborating Agent	Oxidation Product(s)	Isomer Distribution, %	Yield, %	References
Anethole	B_2H_6 -diethyl ether	1- <i>p</i> -Anisyl-1-propanol 1- <i>p</i> -Anisyl-2-propanol	75 25	66	33
$trans$ - p - $CH_3OC_6H_4C(CH_3)=CHCH_3$	B_2H_6 -diethyl ether			72	33
cis - p - $CH_3OC_6H_4C(CH_3)=CHCH_3$	B_2H_6 -diethyl ether			77	33
	B_2H_6 -diethyl ether			—	19, 20
$H_3C=CH(CH_3)_8CO_2C_2H_5$	B_2H_6 -THF			71	61, 66
$H_3C=CH(CH_3)_8CO_2H$	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_3$ BH-THF	$HOCH_2CH_2(CH_3)_8CO_2C_2H_6$		81	66
$H_3C=CH(CH_3)_8CO_2H$	$\left[\begin{array}{c} CH_3 \\ \\ (CH_3)_2CHCH- \end{array} \right]_2$ BH-THF	$HOCH_2CH_2(CH_3)_8CO_2H$		82	38
$CH_3(CH_3)_7CH=CH(CH_3)_8CO_2CH_3$	B_2H_6 -Diglyme	$CH_3(CH_3)_7CH_2CHOH-$ $(CH_3)_8CO_2CH_3$	50	—	39
		$CH_3(CH_3)_7CH_2CHOH-$ $(CH_3)_8CO_2CH_3$	50	—	39

Note: References 59 to 70 are on p. 54.










TABLE XIV
HYDROBORATION-OXIDATION OF DIENES

Diene	Monohydroboration, Reagent	Dihydroboration, Reagent	Oxidation Product(s)	Isomer Distribu- tion, %	Yield, %	References
1,3 Butadiene		B_2H_6 -THF	1,3-Butanediol 1,4-Butanediol	20 80	74	29
2 Methyl 1,3 butadiene		B_2H_6 -THF	1,3-Butanediol 1,4-Butanediol	10 90	78	34
1,2 Pentadiene (<i>cis</i> and <i>trans</i>)		B_2H_6 -THF	2 Methyl 1,3- butanediol	13	69	29
1,4 Pentadiene		B_2H_6 -THF	2 Methyl 1,4- butanediol	87	—	34
2,3 Dimethyl-1,3 butadiene		B_2H_6 -THF	2-Pentene-1-ol (<i>cis</i> and <i>trans</i>)	—	74	34
1,4 Hexadiene		B_2H_6 -THF	1,4 Pentanediol 1,5-Pentanediol	62 38	—	29
1,5 Hexadiene		B_2H_6 -THF	1,4 Pentanediol 1,5 Pentanediol	15 85	—	34
		B_2H_6 -THF	2,3 Dimethyl 1,4- butanediol	—	66	29
		B_2H_6 -D-glucose	1,4 Hexanediol 1,5 Hexanediol	13 87	78	31
		B_2H_6 -THF	6 Hexen-1-ol	—	26	29
		B_2H_6 -THF	5 Hexen-1-ol	—	51	34
		B_2H_6 -THF	1,5 Hexanediol 1,6 Hexanediol	22 69	79	29
		B_2H_6 -THF	2,5 Hexanediol(?) 1,6 Hexanediol	9 —	72	34

Note: References 29 to 70 are on p. 54.

TABLE XIV—Continued
HYDROBORATION-OXIDATION OF DIENES

Diene	Monohydroboration, Reagent	Dihydroboration, Reagent	Oxidation Product(s)	Isomer Distribu- tion, %	Yield, %	Reference
2-Methyl-1,5-hexadiene	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CHCH}- \end{array} \right]_2$ BH-THF		$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$		68	34
Cyclopentadiene	B_2H_6 -diethyl ether		3-Cyclopentene-1-ol		30	33
1,3-Cyclohexadiene	B_2H_6 -THF	B_2H_6 -diethyl ether	<i>trans</i> -1,3-Cyclo-pentanediol 2-Cyclohexen-1-ol 3-Cyclohexen-1-ol	60-65 35-40	41	31, 32
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CHCH}- \end{array} \right]_2$ BH-THF		2-Cyclohexen-1-ol 3-Cyclohexen-1-ol	90 10	70	34
1,4-Cyclohexadiene	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CHCH}- \end{array} \right]_2$ BH-THF		3-Cyclohexen-1-ol		75	34
Bicycloheptadiene	LiBH_4 -BF ₃ -diethyl ether		3-Cyclohexen-1-ol		45	29
	B_2H_6 -THF		<i>cis</i> -Dehydro-norbornol <i>endo</i> -Dehydro-norbornol <i>cis</i> -Dehydro-norbornol <i>endo</i> -Dehydro-norbornol <i>cis</i> -Dehydro-norbornol <i>endo</i> -Dehydro-norbornol	88 12 87 13 87 13	39*	29
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CHCH}- \end{array} \right]_2$ BH-THF		Mixture of diols (†)		64	29

	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \end{array} \right]_n$	BH-Deglyme		72	15
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \end{array} \right]_n$	BH-Deglyme		79	15
1,8 Cyclooctadiene	$(\text{CH}_2)_6\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \end{array} \right]_n$	Mixture of diols	85	34
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \end{array} \right]_n$	BH-THF	$(\text{CH}_2)_6\text{C}=\text{CH}(\text{CH}_2)_4\text{C}(\text{CH}_3)=\text{CH}_2$ $\text{C}(\text{CH}_3)=\text{CH}_2$	85	35
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \end{array} \right]_n$	BH-THF		—	60
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_4\text{CHCH}- \end{array} \right]_n$	BH-THF		—	35

Note: References 69 to 70 are on p. 54

* The yield was determined by vapor phase chromatography.

TABLE XV
MONOHYDROBORATION-OXIDATION OF ACETYLENES

Acetylene	Hydroborating Agent	Oxidation Product	Yield, %	Reference
Acetylene	$\text{C}_4\text{H}_9\text{BH}_2\text{N}^+(\text{CH}_3)_3$	<i>n</i> -Butyraldehyde*	—	36
1-Butyno	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CHCH} \end{array} \right]_2$ BH-Diglymo	<i>n</i> -Hexanal*	—	2
1-Hexyno	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CHCH} \end{array} \right]_2$ BH-Diglymo	3-Hexanone	62	2
3-Hexyno	$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_3)_2\text{CHCH} \end{array} \right]_2$ BH-Diglymo	<i>n</i> -Octanal	70	2

Note: References 59 to 70 are on p. 54.

* The product was identified as the 2,4-dinitrophenylhydrazone.


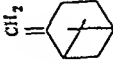
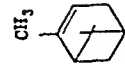
TABLE XVI
ISOMERIZATION-OXIDATION OF ORGANOBORANES

Unsaturated Compound	Hydroborating Agent	Isomerization Time, hr.	Temp., °C.	Oxidation Product(s)	Isomer Distribution, %	Yield, %	References
2-Pentene	NaBH_4 , BF_3 -Diglyme	1	160	1 Pentanol 2 Pentanol	95 4	82	22, 23
1,3-Pentadiene	B_2H_6^*	6	160-175	3 Pentanol	1		
2-Methyl-1-butene	NaBH_4 , BF_3 -Diglyme	4	160	1,5-Pentanediol 2 Methyl 1 butanol	43	83	31
2-Methyl 2-butene	NaBH_4 , BF_3 -Diglyme	4	160	3 Methyl 1 butanol 2 Methyl 1 butanol	1 56	-	23
3 Methyl 1-butene	NaBH_4 , BF_3 -Diglyme	4	160	2 Methyl 1 butanol 3 Methyl 2 butanol	40 2	-	23
2 Hexene	NaBH_4 , BF_3 -Diglyme	1	160	3 Methyl 1 butanol 2 Methyl 1 butanol	58 40	-	23
cis 2-Hexene	NaBH_4 , BF_3 -Diglyme	1	160	3 Methyl 1 butanol 1 Hexanol	59 91	75	22, 23
1,4-Hexadiene	B_2H_6^*	6	160-175	2 Hexanol	6		
1,5-Hexadiene	B_2H_6^*	6	160-175	3 Hexanol	3		
4,4-Dimethyl 2-pentene	NaBH_4 , BF_3 -Diglyme	1	160	2 Hexanol 3-Hexanol	90 6	-	23
				1,5-Hexanediol 1,6-Hexanediol	4 69	82	31
				1,5-Hexanediol 1,6-Hexanediol	31 70	76	31
				4,4-Dimethyl 1-pentanol 4,4-Dimethyl 2-pentanol	30 96	-	23
				2,2-Dimethyl 3-pentanol	2		

Note: References 59 to 70 are on p. 54.

* The conditions for hydroboration were not reported.

TABLE XVI—Continued

Unsaturated Compound	Hydroborating Agent	Isomerization Time, hr.	Temp., °C.	Oxidation Product(s)	Isomer Distribution, %	Yield, %	References
3-Ethyl-2-pentene	$\text{NaBH}_4 \cdot \text{BF}_3 \cdot \text{Diglyme}$	2	160	3-Ethyl-1-pentanol	—	88	23
	$\text{NaBH}_4 \cdot \text{BF}_3 \cdot \text{Diglyme}$	4	160	CH_2OH -cyclohexane	—	—	23
2,4,4-Trimethyl-2-pentene	$\text{NaBH}_4 \cdot \text{BF}_3 \cdot \text{Diglyme}$	1	160	2,4,4-Trimethyl-1-pentanol 2,4,4-Trimethyl-2-pentanol 2,2,4-Trimethyl-3-pentanol	97 1 2	—	23
$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$	$\text{NaBH}_4 \cdot \text{BF}_3 \cdot \text{Diglyme}$	1	160	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ $\text{C}_6\text{H}_5\text{CHOHCH}_2\text{CH}_3$	76 10 14	—	23
Decenes (mixed)	$\text{NaBH}_4 \cdot \text{BF}_3 \cdot \text{Diglyme}$	4	160	1-Decanol	—	70-80	22
	$\text{NaBH}_4 \cdot \text{BF}_3 \cdot \text{Diglyme}$	4	160	$\text{H}-\text{CH}_2\text{OH}$ -cyclohexane	—	80	24, 25
	$\text{NaBH}_4 \cdot \text{BF}_3 \cdot \text{Diglyme}$	4	160	$\text{H}-\text{CH}_2\text{OH}$ -cyclohexane	—	80	24, 25
3-Carene	B_2H_6^*	1	150	10-Hydroxycarene	—	—	70

Note: References 59 to 70 are on p. 54.

* The conditions for hydroboration were not reported.

TABLE XVII
Chromic Acid Oxidation of Organoboranes

Olefin	Hydroborating Agent	Oxidation Product	Yield, %	Reference
Concave	$\text{NaBH}_4\text{-AlCl}_3\text{-Diglyme}$	3 β -Dimethylaminooctanin 6 one	-	46
Cyclohexene	$\text{LiBH}_4\text{-BF}_3\text{-diethyl ether}$	Cyclohexanone	65-63	47
1-Methylcyclopentene	$\text{LiBH}_4\text{-BF}_3\text{-diethyl ether}$	2-Methylcyclopentanone	83	47
1-Methylcyclohexene	$\text{LiBH}_4\text{-BF}_3\text{-diethyl ether}$	2-Methylcyclohexanone	87	47
1-Phenylcyclohexene	$\text{LiBH}_4\text{-BF}_3\text{-diethyl ether}$	2-Phenylcyclohexanone	63	47
α -Pinene	$\text{LiBH}_4\text{-BF}_3\text{-diethyl ether}$	Isopinocampolone	72	47

Note: References 59 to 70 are on p. 54.

REFERENCES FOR TABLES X-XVII

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- ⁶⁰ Newman, Arkell, and Fukunago, *J. Am. Chem. Soc.*, **82**, 2498 (1960).
- ⁶¹ Dulou and Chrétien-Bessière, *Bull. Soc. Chim. France*, **1959**, 1362.
- ⁶² Cristol, Seifert, and Soloway, *J. Am. Chem. Soc.*, **82**, 2351 (1960).
- ⁶³ Dauben, Weinstein, Lim, and Anderson, *Tetrahedron*, **15**, 217 (1961).
- ⁶⁴ Henderson and Huges, *Tetrahedron*, **11**, 226 (1960).
- ⁶⁵ Alvarez and Arreguin, *Chem. & Ind. (London)*, **1960**, 720.
- ⁶⁶ H. C. Brown and K. Keblyas. Unpublished research.
- ⁶⁷ Krug and Boswell, *J. Org. Chem.*, **27**, 95 (1962).
- ⁶⁸ Wolfrom and Whiteley, *Am. Chem. Soc. Meeting, Abstr.*, April 1960, 2D.
- ⁶⁹ Cornforth, *J. Pure and Appl. Chem.*, **2**, 807 (1961).
- ⁷⁰ Arlt, Sheers, and Chamberlain, *Chem. & Ind. (London)*, **1961**, 1409.

CHAPTER 2

HALOCYCLOPROPANES FROM HALOCARBENES

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CONTENTS

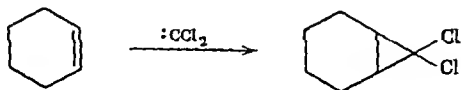
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INTRODUCTION

This chapter reviews methods for the generation of halocarbenes and the reactions of the latter with unsaturated substrates. Chemical transformations of the derived halocyclopropanes are discussed in sufficient detail to demonstrate the synthetic utility of this class. A number of review articles have appeared which discuss carbenes in general and which include some of the halocarbene reactions.^{1-4a} Other chemical reactions that probably proceed by way of dihalocarbenes, such as the Reimer-Tiemann reaction⁵ and the Hofmann isonitrile synthesis,^{6,7} are not included in this review.

The formation of dihalocyclopropanes from dihalocarbenes was first accomplished in 1954 by Doering and Hoffmann,⁸ who used chloroform and



potassium *t*-butoxide to generate the dichlorocarbene. Since that time, a variety of other methods have been developed for the generation of halocarbenes. They are illustrated by the following equations.

¹ Knunyants, Gambaryan, and Rokhlin, *Uspekhi Khim.*, **27**, 1361 (1958) [*C.A.*, **53**, 5107 (1959)].

² Kirmse, *Angew Chem.*, **71**, 537 (1959).

³ Vogel, *Angew Chem.*, **72**, 4 (1960).

⁴ Kirmse, *Angew Chem.*, **73**, 161 (1961).

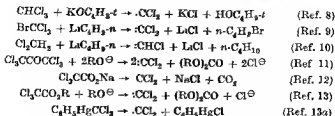
^{4a} Leitlich, *Oesterr. Chemiker Z.*, **61**, 164 (1960).

⁵ Wynberg, *Chem. Revs.*, **60**, 169 (1960).

⁶ Smith and Kalenda, *J. Org. Chem.*, **23**, 1599 (1958).

⁷ Frankel, Feuer, and Bank, *Tetrahedron Letters*, **7**, 5 (1959).

⁸ Doering and Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).



STRUCTURE AND MECHANISM

The halocarbenes are not isolated as such, but the weight of present evidence is that they are in fact low-energy intermediates along the path from the reactants to the products. The postulated structure of the dichlorocarbene intermediate is that shown.^{14,15} The trigonal carbon



atom is considered to have two covalent bonds joining it to the halogen atoms, a pair of electrons having antiparallel spins (singlet state) and an unoccupied *p*-orbital. It is probable that considerable stabilization of this structure is the consequence of overlap of the unshared *p*-electrons of the halogen atoms with the vacant *p*-orbital.¹⁴⁻¹⁶⁻¹⁹ Overlap from fluorine is more effective than from chlorine,²⁰ and as a result difluorocarbene appears to be substantially less reactive than dichlorocarbene.^{19,21-24}

* Müller and Kim, *J. Am. Chem. Soc.*, **81**, 6608 (1959).

¹¹ Closs and Closs, *J. Am. Chem. Soc.*, **81**, 4998 (1959).

¹² Grant and Cassie, *J. Org. Chem.*, **25**, 1452 (1960).

¹³ W. M. Wagner, *Proc. Chem. Soc.*, 1959, 229.

¹⁴ Farham and Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

^{15a} Seyferth, Burlitch, and Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

¹⁶ Skell and Garner, *J. Am. Chem. Soc.*, **75**, 5430 (1953).

¹⁷ Skell and Woodworth, *J. Am. Chem. Soc.*, **78**, 4498 (1956); **79**, 6577 (1957).

¹⁸ Hine and Ehrenson, *J. Am. Chem. Soc.*, **80**, 824 (1958).

¹⁹ Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

²⁰ Skell and Etter, *Chem. & Ind. (London)*, 1958, 624.

²¹ Venkateswarlu, *Phys. Rev.*, **77**, 675 (1950).

²² Hine and Roscup, *J. Am. Chem. Soc.*, **82**, 6115 (1960).

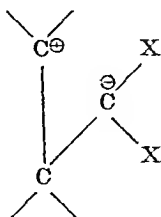
²³ Leard, Andrews, and Barrow, *Trans. Faraday Soc.*, **46**, 803 (1950).

²⁴ Margrave and Wieland, *J. Chem. Phys.*, **21**, 1552 (1953).

²⁵ Duchesne and Burnelle, *J. Chem. Phys.*, **21**, 2005 (1953).

²⁶ Franzen, *Chem. Ber.*, **95**, 1964 (1962).

The addition of dihalocarbenes to olefins has been shown by Skell¹⁴ and by Doering²⁵ to be a stereospecific *cis* addition. (See also pp. 65-66.) This work supports the view that the addition is a concerted three-center process. To be stereospecific, a stepwise process leading to a charge-separated intermediate would require that this intermediate collapse to



the cyclopropane faster than rotation could occur about a C—C single bond. The stereospecific character of the reaction also supports the view that dihalocarbenes exist in the singlet ground state.²⁶⁻²⁸

PREPARATION OF HALOCARBENES

Alkoxide-Haloform Reactions. In 1854, Williamson studied the reactions of chloroform with ethanolic sodium ethoxide and isolated triethyl orthoformate as the principal product.²⁹ This study was followed by a number of others that dealt with the reactions of haloforms with alkoxides and alcohols^{30,31} and with heterocyclic nitrogen compounds.³²⁻³⁵ In 1862, Geuther³⁶ postulated a dichlorocarbon intermediate, a concept generally accepted by chemists.³⁷⁻⁴³

²⁵ Doering and LaFlamme, *J. Am. Chem. Soc.*, **78**, 5447 (1956).

²⁶ Woodworth and Skell, *J. Am. Chem. Soc.*, **81**, 3383 (1959).

²⁷ Etter, Skovronek, and Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

²⁸ Parham and Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954).

²⁹ Williamson, *Proc. Roy. Soc. (London)*, **7**, 135 (1854).

³⁰ Bassett, *Ann.*, **132**, 54 (1864).

³¹ Gorboff and Kessler, *J. Prakt. Chem.*, [2] **41**, 224 (1890).

³² Ciamician, *Ber.*, **37**, 4231 (1904).

³³ Magnanini, *Ber.*, **20**, 2608, (1887); *Gazz. Chim. Ital.*, **17**, 246 (1887).

³⁴ Zanetti and Levi, *Gazz. Chim. Ital.*, **24** [II], 111 (1894).

³⁵ Bocchi, *Gazz. Chim. Ital.*, **30** [I], 89 (1900).

³⁶ Geuther, *Ann.*, **123**, 121 (1862).

³⁷ Ciamician and Dennstedt, *Ber.*, **14**, 1153 (1881).

³⁸ Urbain, *Bull. Soc. Chim. France*, [4] **51**, 853 (1932).

³⁹ Tchakirian, *Bull. Soc. Chim. France*, [4] **51**, 846 (1932).

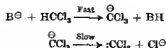
⁴⁰ Urbain, *Bull. Soc. Chim. France*, [4] **53**, 637 (1933).

⁴¹ Meesler, *Monatsh. Chem.*, **29**, 573 (1908).

⁴² Thiele and Dent, *Ann.*, **302**, 273 (1898).

⁴³ Nef, *J. Am. Chem. Soc.*, **30**, 645 (1908).

Interest in this reaction was renewed in 1950 when Hine published the first of a series of papers in which he elucidated the mechanism of haloform-base reactions.^{16 17,44-47} Hine postulated an initial fast attack of base on chloroform to give the trichloromethyl anion and the conjugate base. The trichloromethyl anion then slowly decomposed to give dichlorocarbene.⁴⁷



Further studies revealed that haloforms having two fluorine atoms tended to form difluorocarbene by a concerted loss of a proton and a halide ion.⁴⁴



Hine and his co-workers have made extensive studies related to the hydrolysis of haloforms and the formation of halomethylenes from haloforms. The relative rates of formation of carbanions from haloforms is $\text{CHI}_3 \sim \text{CHBr}_3 > \text{CHBr}_2\text{Cl} > \text{CHBrCl}_2 \sim \text{CHCl}_2\text{I} > \text{CHBr}_2\text{F} > \text{CHCl}_2\text{F} > \text{CHBrClF} > \text{CHCl}_2\text{F}$, showing that α -halogen substituents facilitate carbanion formation in the order $\text{I} \sim \text{Br} > \text{Cl} > \text{F}$.⁴⁵ The kinetics of hydrolysis of a number of haloforms in dioxane-water established the following order $\text{CHBrClF} \gg \text{CHBrCl}_2 > \text{CHBr}_2\text{Cl} \sim \text{CHCl}_2\text{I} > \text{CHBr}_3 > \text{CHCl}_3 \gg \text{CHF}_3$.

The relative reactivities of the haloforms toward hydrolysis in aqueous solution have been correlated in terms of an equation based on the dihalomethylene reaction.^{18 46} This equation uses the known carbanion formation rate constants and contains parameters for (1) the relative abilities of the various halogens to stabilize dihalomethylenes, (2) the relative ease with which halogens are separated as anions from the intermediate trihalomethyl anions, and (3) the carbanion character of the transition state for dihalomethylene formation. From the values of these parameters, halogens appear to facilitate dihalomethylene formation from CX_3^\ominus in the order $\text{F} \gg \text{Cl} > \text{Br} > \text{I}$. This order is attributed to the relative abilities of the halogens to supply electrons to the carbon atom. The parameters for the differences between the abilities of halogen to separate as anions ($\text{Br} > \text{I} > \text{Cl}$) are smaller and probably less significant.

The formation of dichlorocyclopropanes from chloroform, an alkoxide, and an olefin is an excellent preparative procedure.⁸ Potassium *t*-butoxide

⁴⁴ Hine and Langford, *J. Am. Chem. Soc.*, **79**, 5497 (1957).

⁴⁵ Hine, Burke, Hine, and Langford, *J. Am. Chem. Soc.*, **79**, 1406 (1957).

⁴⁶ Hine, Dowell, and Singley, *J. Am. Chem. Soc.*, **78**, 478 (1956).

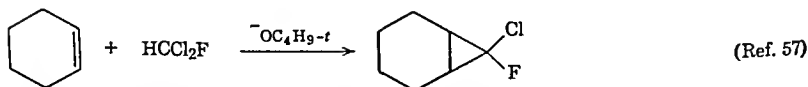
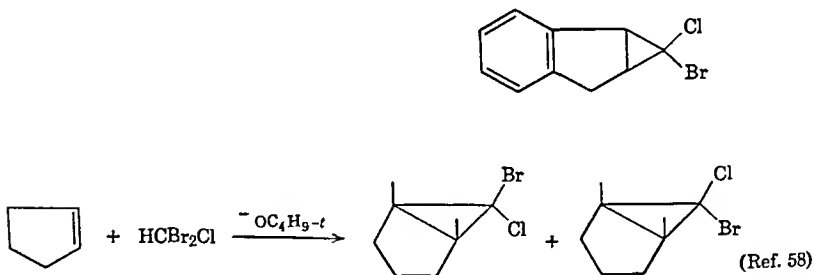
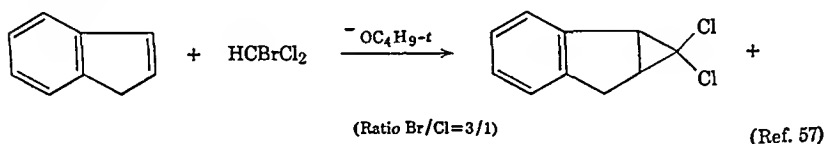
⁴⁷ Hine and Dowell, *J. Am. Chem. Soc.*, **76**, 2888 (1954).

⁴⁸ Hine and Prosser, *J. Am. Chem. Soc.*, **80**, 4282 (1958).

is the base of choice. Other alkoxides can be employed, but usually with lower yields. A competing reaction between dichlorocarbene and the alcohol formed in the reaction lowers the yield of cyclopropane, and this side reaction is slower with the more hindered alcohols. Negatively substituted olefins do not give cyclopropanes but react with the intermediate trihalomethyl anion.^{48a}

The reaction of bromoform with potassium *t*-butoxide and an olefin leads to dibromocyclopropanes in good yield.^{8,49,50} Fluoroform and iodoform do not, however, lead to the formation of analogous products; the iodoform is reduced to methylene iodide.⁵⁰

The hydrolysis of mixed haloforms has been studied,^{44,46,48,51-58} and mixed haloforms have been used in the preparation of cyclopropanes as illustrated by the accompanying equations.



^{48a} Bruson, Neiderhauser, Riener, and Hester, *J. Am. Chem. Soc.*, **67**, 601 (1945).

⁴⁹ Skell and Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).

⁵⁰ Parham, Reiff, and Swartzentruber, *J. Am. Chem. Soc.*, **78**, 1437 (1956).

⁵¹ Skell and Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

⁵² Hine and Porter, *J. Am. Chem. Soc.*, **82**, 6118 (1960).

⁵³ Hine, Ketley, and Tanabe, *J. Am. Chem. Soc.*, **82**, 1398 (1960).

⁵⁴ Hine and Tanabe, *J. Am. Chem. Soc.*, **80**, 3002 (1958).

⁵⁵ Hine and Porter, *J. Am. Chem. Soc.*, **79**, 5493 (1957).

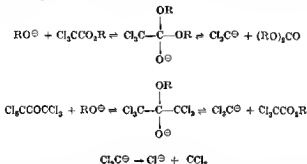
⁵⁶ Hine and Ketley, *J. Org. Chem.*, **25**, 606 (1960).

⁵⁷ Parham and Twelves, *J. Org. Chem.*, **22**, 7

⁵⁸ Skell and Sandler, *J. Am. Chem. Soc.*, **80**,

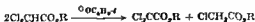
The reaction of olefins with dihalomethanes and an alkoxide leads to monohalocyclopropanes,⁵⁹⁻⁶¹ but the yields of adducts are poor. The preferred method for generating monohalocarbenes is the reaction of dihalomethanes with an alkylolithium (see p. 63).

Alkoxide-Trihalocarbon Carbonyl Reaction. The reaction of esters of trichloroacetic acid^{13, 62, 63} or hexachloroacetone^{11, 64} with alkoxides in the presence of olefins leads to good yields of dichlorocyclopropanes. No alcohol is formed in these reactions and the use of hindered alkoxides is not necessary.



The dialkyl carbonate formed may be separated from the product by extraction with sulfuric acid or by distillation. Of the two equivalents of dichlorocarbene available from hexachloroacetone only one is utilized effectively, probably because some is lost through reaction with alkoxide ion (see p. 59).

No comparable studies using trihaloacetates or haloacetones other than chloro compounds have been reported. Esters of dihaloacetic acids do not lead to monohalocarbenes. Instead derivatives of dihalocarbenes result, possibly as a consequence of an initial base-catalyzed disproportionation.^{62, 63}



Pyrolytic Reactions. The thermal decomposition of salts of trihaloacetic acids in 1,2-dimethoxyethane or bis-(β -methoxyethyl) ether under

⁵⁹ Alexander, Herrick, and Roder, *J. Am. Chem. Soc.*, **72**, 2760 (1950).

⁶⁰ Volpin, Kuranov, and Dulova, *Tetrahedron*, **8**, 33 (1960).

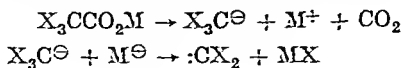
⁶¹ Dennstedt and Zimmermann, *Ber.*, **18**, 3318 (1885).

⁶² Parham, Loew, and Schweizer, *J. Org. Chem.*, **24**, 1900 (1959).

⁶³ Parham and Loew, *J. Org. Chem.*, **23**, 1765 (1958).

⁶⁴ Kadaba and Edwards, *J. Org. Chem.*, **25**, 1631 (1960).

reflux in the presence of an olefin leads to the formation of dihalocyclopropanes.^{12,65,66} These reactions are thought to occur as follows.



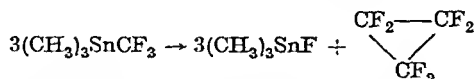
The yields of adducts are comparable to those obtained from haloforms. The method has been used for the generation of difluorocarbene⁶⁵ and is of special interest since it can be employed for the preparation of adducts of carbene acceptors that are sensitive to bases.

Silver trichloroacetate undergoes a side reaction forming carbon monoxide and trichloroacetyl chloride.⁶⁷⁻⁶⁹

Another useful pyrolytic reaction is that of phenyltribromomethyl- and phenyltrichloromethyl-mercury which, when heated in benzene, give the corresponding dihalonorcarane adduct with cyclohexene in 88% yield.^{13a}

A number of other pyrolytic procedures that may proceed via a dihalocarbene have been reported.⁷⁰⁻⁷⁷ These pyrolyses have been carried out in the absence of a carbene acceptor and result in products that could be derived from polymerization, dimerization, or disproportionation of several possible intermediates.

Thermal decomposition of trimethyltrifluoromethyltin appears to proceed via difluoromethylene since pyrolysis, alone or with tetrafluoroethylene, gives perfluorocyclopropane in high yield.⁷⁸



Thermal decomposition of certain halogeno-alkyl silicon compounds may also produce carbenes. Dichloronorcarane was obtained in 60% yield by allowing cyclohexene to react with trichloromethylsilicon trichloride at 250°. ⁷⁹

⁶⁵ Birchall, Cross, and Haszeldine, *Proc. Chem. Soc.*, 1960, 81.

⁶⁶ Wagner, Kloosterziel, and van der Ven, *Rec. Trav. Chim.*, 80, 740 (1961).

⁶⁷ Badea and Nenitzescu, *Angew Chem.*, 72, 415 (1960).

⁶⁸ Ioan, Badea, Cioranescu, and Nenitzescu, *Angew Chem.*, 72, 416 (1960).

⁶⁹ Beckurts and Otto, *Ber.*, 14, 576 (1881).

⁷⁰ Chambers, Clark, and Willis, *J. Am. Chem. Soc.*, 82, 5298 (1960).

⁷¹ Semeluk and Bernstein, *J. Am. Chem. Soc.*, 79, 46 (1957).

⁷² Haszeldine and Young, *Proc. Chem. Soc.*, 1959, 394.

⁷³ Atkinson and Atkinson, *J. Chem. Soc.*, 1957, 2086.

⁷⁴ Atkinson, *J. Chem. Soc.*, 1952, 2684.

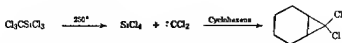
⁷⁵ Park, Benning, Downing, Laucius, and McHarness, *Ind. Eng. Chem.*, 39, 354 (1947).

⁷⁶ Fink and Bonilla, *J. Phys. Chem.*, 37, 1135 (1933).

⁷⁷ Hodgins and Haines, *Can. J. Chem.*, 30, 473 (1952).

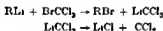
⁷⁸ Clark and Willis, *J. Am. Chem. Soc.*, 82, 1898 (1960).

⁷⁹ Bevan, Haszeldine, and Young, *Chem. & Ind. (London)*, 1961, 789.



The reported isolation⁴⁰ of dichlorocarbene by pyrolysis of carbon tetrachloride has not been confirmed, however, difluoromethylene has been trapped at low temperature and identified as a product obtained by passage of radiofrequency discharge through certain fluorocarbons.⁴¹

Alkyl lithium-Halocarbon Reactions. The reaction of an alkyl lithium with certain carbon tetrahalides in the presence of an olefin gives derivatives of dihalocyclopropanes.⁹ For example, dichloronorcaradiene has been prepared in 91% yield from bromotrichloromethane and cyclohexene.⁹ The reaction proceeds by initial halogen-lithium exchange followed by loss of lithium halide to give the dihalocarbene. Difluorocarbene has also been prepared by this method from dibromodifluoromethane.⁴²

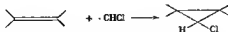
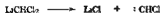


Dihalocarbenes can also be prepared from an alkyl lithium and a haloform.⁴³



However, when this reaction was carried out in the presence of olefins relatively low yields of adducts resulted, and the reaction appears to be of little synthetic value.

The most important application of the alkyl lithium-halocarbon reaction is its use for the synthesis of monochlorocarbene.^{10, 43} Closs and his co-workers have shown that this procedure is the best method for the synthesis of many monochlorocyclopropanes.



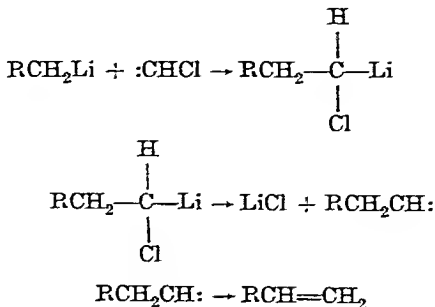
⁴⁰ Schneisser and Schröter, *Angew Chem*, **72**, 349 (1960).

⁴¹ Mastrangelo, *Abstr*, *140th Meeting, Am Chem Soc*, September, 1961, p. 6V.

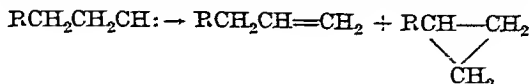
⁴² Franzen, *Angew Chem*, **72**, 569 (1960).

⁴³ Closs and Closs, *J Am Chem. Soc*, **82**, 5723 (1960).

The predominant side reaction observed is the formation of the olefin $\text{RCH}=\text{CH}_2$ from the alkyllithium RCH_2Li . The olefin is thought to result from the reaction of monochlorocarbene with RCH_2Li followed by loss of lithium chloride and a 1,2-hydride shift.



Along with the olefin $\text{RCH}=\text{CH}_2$, some cyclopropane corresponding to an intramolecular insertion reaction of $\text{RCH}_2\text{CH:}$ is also formed.^{83a} When



methylene chloride is added to excess alkyllithium, the reaction of the alkyllithium with chlorocarbene predominates and terminal olefins are formed in high yield.^{10,83}

REACTIONS OF HALOCARBENES

With Alkenes, Cycloalkenes, and Alkynes. The principal reaction of halocarbenes with olefins is addition to form halocyclopropanes, and the order of reactivity of carbenes appears to be $\text{CH}_2 > \text{CHCl} > \text{CCl}_2 > \text{CBr}_2 > \text{CF}_2$.^{14,60,83-87} This order is consistent with added stabilization provided by overlap of the unshared *p*-electrons of the halogen with the vacant *p*-orbital of the carbene.

The halocarbenes are electrophilic in character, and the relative rates of their additions to carbon-carbon double bonds generally increase with increasing alkyl substitution at the olefin function.^{14,49,83,85} Steric factors appear to be less important in this respect than electronic factors.^{14,50,87,89}

⁸² Closs, *Abstr. 135th Meeting, Am. Chem. Soc., Sept., 1960*, p. 9P.

⁸⁴ Doering and Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1959).

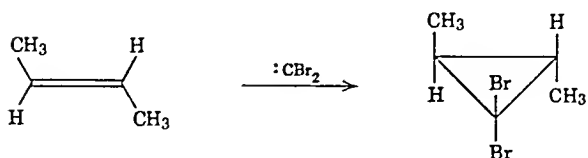
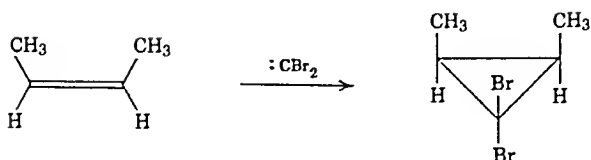
⁸⁵ Doering, Buttery, Laughlin, and Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

⁸⁶ Ledwith and Bell, *Chem. & Ind. (London)*, 1959, 459.

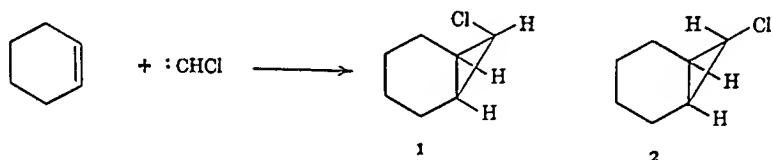
⁸⁷ Closs and Schwartz, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

⁸⁸ Woodworth and Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957).

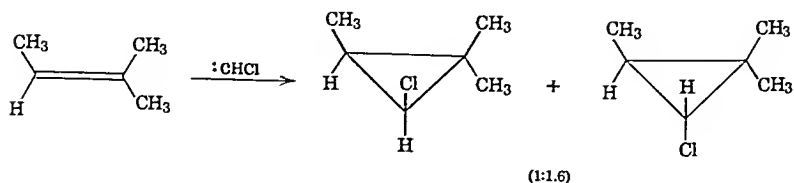
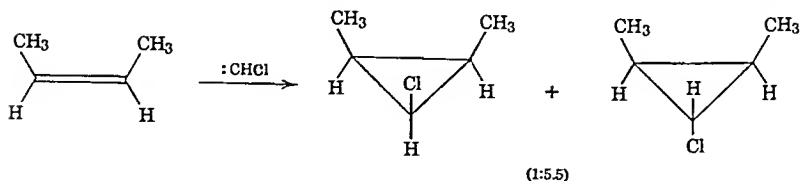
⁸⁹ Parham and Wright, *J. Org. Chem.*, **22**, 1473 (1957).



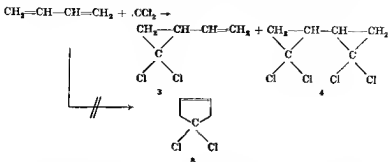
The reaction of monochlorocarbene with cyclohexene gives two isomers that were tentatively assigned the *endo* 1 and *exo* 2 structures.⁸³



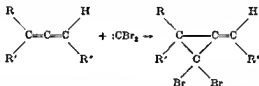
Differences in *cis/trans* ratios are also noted with olefins that react more slowly than cyclohexene, and it seems probable that steric factors alone can provide only a partial explanation of these observations. For example, *cis/trans* ratios for the products from monochlorocarbene and *cis*-2-butene and 2-methyl-2-butene are 1:5.5 and 1:1.6, respectively.⁸³



Dichloro- and dibromo-carbene add to 1,3-dienes to give vinylcyclopropanes,^{86 88 89,91,92} there is no evidence for 1,4-addition. Thus dichloro-carbene reacts with butadiene to give 3 and 4 but not 5.⁹¹



Dibromocarbene⁹³ adds similarly to 1,2-dienes to give methylenecyclopropane derivatives (40–60% yield). Such additions are reported to occur exclusively at the more highly alkylated double bond.



Hydrocarbons containing both double and triple bonds have been treated with dihalocarbenes. The only products reported from the reactions of dichloro- and dibromo-carbene with conjugated eneynes were those derived by additions to the carbon-carbon double bonds.^{94 95}

Dihalocarbenes add to internal triple bonds to form dihalocyclopropenes,^{96–98} which have been useful intermediates for the preparation of cyclopropenones. Attempts to prepare halocyclopropenes from terminal acetylenes have been unsuccessful.^{99,100}

⁹¹ Orehin and Hornick, *J. Org. Chem.*, **24**, 139 (1959).

⁹² Shono and Oda, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **90**, 1200 (1959).

⁹³ Ball and Lander, *Proc. Chem. Soc.*, **1961**, 249.

⁹⁴ D'yakonov, Favorskaya, Danilkina, and Anvinin, *J. Gen. Chem. USSR (English Transl.)* **30**, 3475 (1960) [*C.A.*, **55**, 19814 (1961)].

⁹⁵ Vo-Quang and Cadot, *Compt. Rend.*, **252**, 3827 (1961).

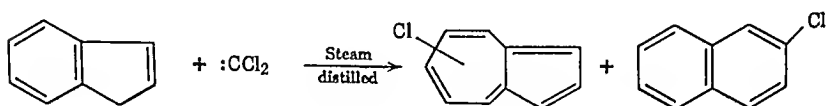
⁹⁶ Breslow and Peterson, *J. Am. Chem. Soc.*, **82**, 4428 (1960).

⁹⁷ Volpin, Korshkov, and Kuranov, *Izv. Akad. Nauk SSSR*, **1960**, 560 [*C.A.*, **53**, 21709 (1959)].

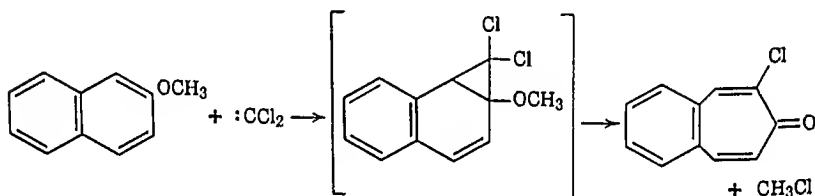
⁹⁸ Kuranov, Volpin, and Korshkov, *J. Gen. Chem. USSR (English Transl.)*, **30**, 2855 (1960) [*C.A.*, **55**, 16473 (1961)].

With Aromatic Carbon-Carbon Double Bonds. Dichlorocarbene reacts only with difficulty with aromatic double bonds, and many reactions involving dihalocarbene have been effected by using benzene as solvent.^{60,86,89,99,100} Reaction generally occurs with electron-rich aromatic compounds.

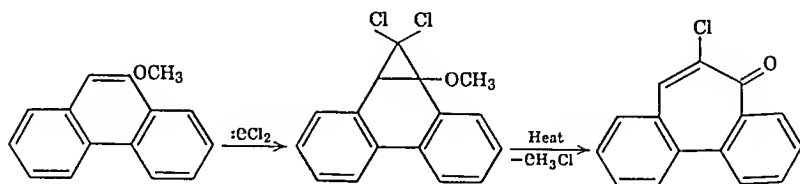
The formation of a small amount of a chloroazulene from indene and dichlorocarbene results from attack of the carbene on an aromatic double bond.¹⁰¹



Chlorotropones are produced when dichlorocarbene reacts with alkoxy-naphthalenes.¹⁰⁰



With 9-methoxyphenanthrene, the intermediate dichlorocyclopropane was isolated in 52% yield and converted by heat to the dibenzchlorotroponone in high yield.



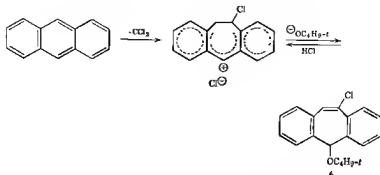
No report has yet been made of the interaction of dihalocarbenes with naphthalene or phenanthrene, but anthracene reacts with dichlorocarbene to form a chlorotropilium salt that is converted to 6 by the action of base.¹⁰² Treatment of 6 with acid regenerates the tropilium salt.

⁹⁹ Closs and Closs, *Tetrahedron Letters*, **10**, 38 (1960).

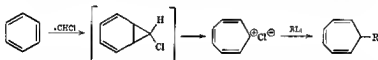
¹⁰⁰ Parham, Bolon, and Schweizer, *J. Am. Chem. Soc.*, **83**, 603 (1961).

¹⁰¹ Parham and Reiff, *J. Am. Chem. Soc.*, **77**, 1177 (1955).

¹⁰² Murray, *Tetrahedron Letters*, **7**, 27 (1960).

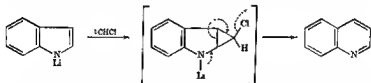


Monochlorocarbene, which is more reactive than dichlorocarbene, reacts readily with benzene to give derivatives of cycloheptatriene.⁶⁰⁻⁶⁹ The



reaction of methyllithium with lithium phenoxide in methylene chloride occurs in a similar manner and yields 2-methyl-3,5-cycloheptadienone.¹⁰³ A variety of substituted phenoxides reacts to form similar products.

Many ring expansions of pyrroles^{35, 37, 59, 61, 104-106} and indoles^{39, 108} to form pyridines and quinolines have been reported. An example is the conversion of indole to quinoline by the action of methyllithium and methylene chloride.¹⁰⁶



With Carbon-Nitrogen Double Bonds. The only reaction of this type that has been reported is that of dichlorocarbene with benzalaniline to form 7.^{64, 107} The product is rapidly hydrolyzed to *N*-phenyl- α -chloro-phenylacetamide.

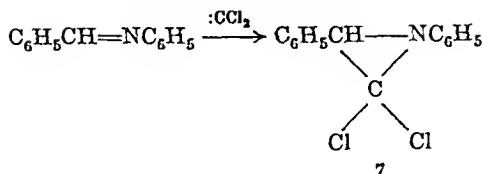
¹⁰³ Closs and Closs, *J. Am. Chem. Soc.*, **83**, 599 (1961).

¹⁰⁴ Casanovic and Dennstedt, *Ber.*, **15**, 1172 (1883).

¹⁰⁵ Casanovic and Silber, *Ber.*, **20**, 191 (1887).

¹⁰⁶ Closs and Schwartz, *J. Org. Chem.*, **26**, 2883 (1961).

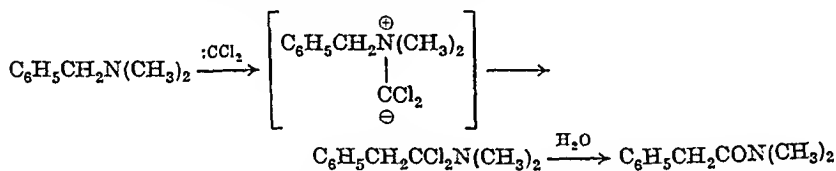
¹⁰⁷ Fields and Sandri, *Chem. & Ind. (London)*, 1953, 1238.



Miscellaneous Reactions. Detailed review of the many other reactions of halocarbenes is beyond the scope of this chapter. Some of the most important ones are summarized here primarily to provide a convenient key to the literature on this aspect of halocarbene chemistry.

Early work showed that carbon monoxide and orthoformates were formed from dihalocarbenes and alcohols.^{29-31,103} Modern techniques have led to the identification of many other products from these reactants.^{51,53-55,109,110}

Secondary and tertiary amines react with dichlorocarbene to give amides after hydrolysis of the intermediates.^{7,111} Primary amines react with



dichlorocarbene in non-aqueous media to form isocyanides.^{6,112} This observation supports the proposed mechanism of the Hofmann isocyanide synthesis.^{6,7}

Triphenylphosphine reacts with dichlorocarbene to give dichlorophosphine methylene, which has been used in the Wittig reaction to prepare terminal dichloroolefins, $\text{RCH}=\text{CCl}_2$.^{113,114} Wittig reagents have been similarly prepared from monochlorocarbene^{115,116} and difluorocarbene.⁸²

Difluorocarbene has been allowed to react with a number of anions to give difluoromethyl derivatives.¹¹⁷ For instance diethyl phenyldifluoromethylmalonate was obtained in 80% yield by allowing difluorocarbene to react with the sodium salt of diethyl phenylmalonate.¹¹⁷

¹⁰⁸ Nef, *Ann.*, **308**, 329 (1899).

¹⁰⁹ Hine and Tanabe, *J. Am. Chem. Soc.*, **79**, 2654 (1957).

¹¹⁰ Hine, Pollitzer, and Wagner, *J. Am. Chem. Soc.*, **75**, 5607 (1953).

¹¹¹ Saunders and Murray, *Tetrahedron*, **6**, 88 (1959).

¹¹² Krapcho, *J. Org. Chem.*, **27**, 1089 (1962).

¹¹³ Speziale, Marco, and Ratts, *J. Am. Chem. Soc.*, **82**, 1260 (1960).

¹¹⁴ Speziale, Ratts, and Marco, *Abstr.*, 140th Meeting, Am. Chem. Soc., September 1961, p. 35Q.

¹¹⁵ Seyferth, Grim, and Read, *J. Am. Chem. Soc.*, **82**, 1510 (1960).

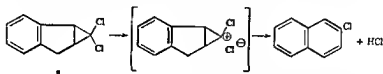
¹¹⁶ Seyferth, Grim, and Read, *J. Am. Chem. Soc.*, **83**, 1617 (1961).

¹¹⁷ Shen, Lucas, and Sarett, *Tetrahedron Letters*, **2**, 43 (1961).

REACTIONS OF HALOCYCLOPROPANES

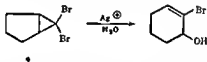
The halocyclopropanes undergo transformations leading either to ring expansion, chain lengthening, or formation of a second cyclopropane ring and are thus valuable synthesis intermediates.

The first example of ring expansion was the quantitative conversion of the cyclopropane derivative **8** to 2-chloronaphthalene⁴⁰

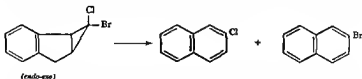


Similar reactions starting with a variety of substituted indenenes have been carried out^{40, 47, 48, 101}. Preliminary studies have shown that the rates of these reactions are unaffected by added alkali⁴⁰ but are increased by added silver ion⁴⁸.

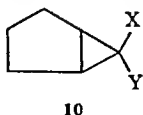
The bicyclo [3 1 0] system of **9** is 200 times as reactive as the analogous [4 1 0] system in dibromonorcaradiene⁴⁸. The reason for this greatly enhanced rate is thought to be the relief of the greater strain in the [3.1.0] system.



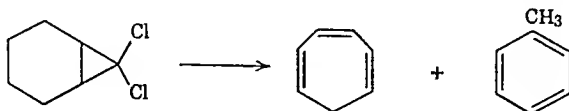
An interesting steric requirement for these ring expansion reactions was noted for mixed halides obtained from indene⁴⁷. The ratio of 2-chloro- and 2-bromo-naphthalene obtained was approximately 1:1.



The α - and β -isomers (*endo-exo*) of 2-bromo-2-chlorobicyclo[3.1.0]hexane (**10**, X = Cl, Y = Br) have been isolated,⁴⁸ but their absolute configurations have not been determined.



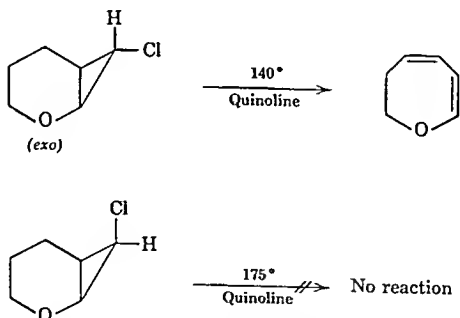
Dihalocyclopropanes are decomposed thermally, and the ease of ring expansion is a function of structure. Dichloronorcaradiene gives cycloheptatriene and toluene by pyrolysis at 490° .¹¹⁸



The analogous 2-oxa-7,7-dichlorobicyclo[4.1.0]heptane gives 3-chloro-6,7-dihydroöxepine at 140° .¹¹⁹



The two isomers of 2-oxa-7-chloronorcaradiene differ strikingly in their reactivity. One, tentatively identified as *exo*, gives the dihydroöxepine by reaction at 140° in quinoline. Under these conditions the other, supposedly *endo*, isomer is unaffected.



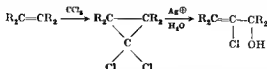
It is probable that relief of strain, relative stability of possible intermediate ions, and anchimeric assistance by hetero atoms all may be involved in determining the ease with which a particular halocyclopropane undergoes this type of reaction.

Similar reactions applied to halocyclopropanes bearing aliphatic rather than cycloaliphatic substituents produce a chain-lengthening process by

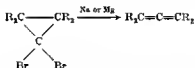
¹¹⁸ Winberg, *J. Org. Chem.*, **24**, 264 (1959).

¹¹⁹ Schweizer and Parham, *J. Am. Chem. Soc.*, **82**, 4085 (1960).

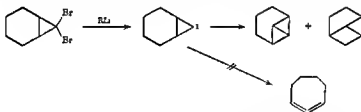
insertion of a new atom *between* the doubly bonded atoms of the original olefin ⁵³



A generally applicable method of chain lengthening is the conversion of halocyclopropanes to allenes. This reaction, discovered by Doering, involves reaction of the dibromocyclopropane with sodium or magnesium ¹²⁰. The yields of allenes are quite high, however, some isomeric



products are also formed ¹²⁰⁻¹²². The reaction has been extended under different conditions to dichlorocyclopropanes ^{123,124}. High yields of purer allenes are obtained when dibromocyclopropanes are allowed to react with an alkyl lithium, ^{125,126} and this method is convenient for the synthesis of cyclic and acyclic allenes. These reactions with alkyl lithiums have been shown to involve carbene intermediates by studies with dibromonorcaradiene.



Collapse of the intermediate bicyclic carbene to the cyclic seven-membered ring allene is sterically unfavorable; intramolecular insertion to give highly strained bicyclic systems results. ^{125,127}

¹²⁰ Doering and LaFlemme, *Tetrahedron*, **2**, 75 (1958)

¹²¹ Gardner and Narayana, *J. Org. Chem.*, **26**, 3518 (1961)

¹²² Skattebøl, *Tetrahedron Letters*, **5**, 167 (1961)

¹²³ Ball and Landor, *Proc. Chem. Soc.*, **1961**, 143

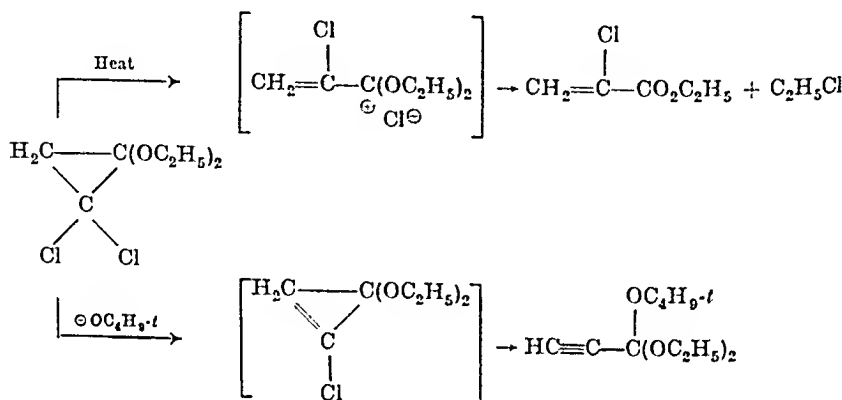
¹²⁴ Logan, *Tetrahedron Letters*, **5**, 173 (1961)

¹²⁵ Moore and Ward, *J. Org. Chem.*, **25**, 2073 (1960).

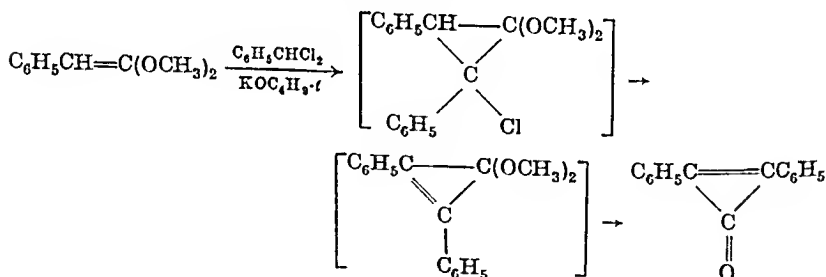
¹²⁶ Moore, Ward, and Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

¹²⁷ Moore and Ward, *Chem. & Ind. (London)*, **1961**, 594

The 2,2-dihalocyclopropanone acetals, prepared by addition of dihalocarbene to ketene acetals, may be converted to α -chloroacrylic esters by heat or to orthopropiolates by base.¹²⁸



The propiolate reaction is thought to proceed through the cyclopropene. Additional evidence in support of this view is the reaction of phenylchlorocarbene with phenylketene acetal and transformation of the intermediate to 2,3-diphenylcyclopropenone.¹²⁹



EXPERIMENTAL PROCEDURES

7,7-Dichlorobicyclo[4.1.0]heptane. *A.* (Using chloroform as the carbene source.⁸) A stirred mixture of 1.5 l. of dry *t*-butyl alcohol (distilled from aluminum *t*-butoxide) and 60 g. (1.5 moles) of potassium metal is allowed to react at the boiling point of the alcohol. The alcohol is then removed by distillation and the residue is dried at 150–160°/1–2 mm. for 2 hours. The dried solid is powdered manually and covered with 1.5 l. of cyclohexene. To the resulting mixture, cooled in an ice bath,

¹²⁸ McElvain and Weyna, *J. Am. Chem. Soc.*, **81**, 2579 (1959).

¹²⁹ Breslow, Haynie, and Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959).

reagent grade methylene chloride (17 g., 0.2 mole) under an atmosphere of nitrogen. The mixture is hydrolyzed, the organic layer separated, washed, and dried over magnesium sulfate. Distillation gives 8.8 g. (67%) of 1-chloro-2,2,3,3-tetramethyleyclopropane, b.p. $72^{\circ}/105$ mm., n_D^{20} 1.4458.

2-Oxa-7-chlorobicyclo[4.1.0]heptane.¹¹⁹ Commercial *n*-butyllithium (3.54 moles) in heptane is added dropwise during 4 hours to a cold (-10° to -20°) mixture of dry dihydropyran (378 g., 4.5 moles) and dry methylene chloride (382 g., 4.5 moles). The mixture is allowed to warm to room temperature and is stirred overnight. Water (600 ml.) is added, the mixture is filtered, and the organic layer separated. The aqueous layer is extracted three times with 400-ml. portions of petroleum ether (b.p. $30-60^{\circ}$), and the combined organic layers are dried over anhydrous magnesium sulfate. Distillation furnishes 134 g. (28%) of a mixture of the racemic isomers of 2-oxa-7-chlorobicyclo[4.1.0]heptane, b.p. $45-48^{\circ}/3-1.5$ mm., n_D^{25} 1.4798–1.4879. The mixture is separated by fractionation into *endo*-2-oxa-7-chloronorecarane (b.p. $34.0^{\circ}/1.1$ mm., n_D^{25} 1.4765) and *exo*-2-oxa-7-chloronorecarane (b.p. $48^{\circ}/1.5$ mm., n_D^{25} 1.4873).

2,7-Di-*t*-butyltropone.¹⁰³ Methylithium (0.41 mole) in diethyl ether (230 ml.) is added over a period of 2.5 hours to a solution of 2,6-di-*t*-butylphenol (48 g., 0.23 mole) in 250 ml. of methylene chloride at room temperature. After hydrolyzing in ice water, the organic layer is washed consecutively with dilute hydrochloric acid, aqueous sodium bicarbonate, and water. Removal of the solvent and distillation give 34.5 g. (0.17 mole) of 2,6-di-*t*-butylphenol (b.p. $57-58^{\circ}/0.15$ mm.) and crude 2,7-di-*t*-butyltropone (b.p. $76-82^{\circ}/0.15$ mm.). Redistillation of the crude product yields 9.1 g. of 2,7-di-*t*-butyltropone boiling at $67-70^{\circ}/0.10$ mm. (70% based on recovered 2,6-di-*t*-butylphenol). Recrystallization of the tropone twice from pentane gives an analytical sample, m.p. 70.5° .

TABULAR SURVEY

Tables I through IV encompass the reactions of dihalocarbenes. Monohalocarbenes are surveyed in Table V. The tables are arranged according to the nature of the halide, in the following order: chlorine, bromine, iodine, fluorine. The acceptors in each table under a given halocarbene are arranged in order of increasing number of carbon atoms.

Where more than one reference is cited, the experimental data are taken from the experiment reporting the highest yield; this reference is cited first. Where the yield is not given, a dash is placed in the yield column.

The literature through November 1, 1961, and a few more recent references are included in the text and tables.

TABLE I


REACTIONS OF DICHLOROCARBENE WITH ALKENES, ALKYNES, AND CYCLOALKENES

Carbene Acceptor	Carbene Precursor	Base	Product(s)	Yield, %	Refs
2 Methyl-1-propene	CHCl_3	KOC_4H_9 , t	1,1-Dichloro-2,2-dimethylcyclopropane	65	8, 63, 84
	$\text{CCl}_3\text{CO}_2\text{C}_4\text{H}_9$	NaOCH_3	1,1-Dichloro-2,2-dimethylcyclopropane	76	13
	$\text{CCl}_3\text{CO}_2\text{C}_2\text{H}_5$, t	KOC_4H_9 , t	1,1-Dichloro-2,2-dimethylcyclopropane	86	13, 63
	$\text{CCl}_3\text{CO}_2\text{K}$	*	<i>Di t</i> -butyl carbonate	89	66
	$\text{CHCl}_2\text{CO}_2\text{C}_4\text{H}_9$, t	KOC_4H_9 , t	1,1-Dichloro-2,2-dimethylcyclopropane	13	63
1,3-Butadiene	$\text{CHCl}_2\text{CO}_2\text{C}_4\text{H}_9$, t	KOC_4H_9 , t	<i>Di t</i> -butyl carbonate	16-20	
	$(\text{CH}_3)_3\text{COCl}$ CHCl_3	KOC_4H_9 , t	Hexa <i>t</i> -butyl mellitate	3	
			1,1-Dichloro-2,2-dimethylcyclopropane	55	62
		KOC_4H_9 , t	<i>t</i> -Butyl trichloroacetate	5	
			1,1-Dichloro 2 vinylcyclopropane	51	
1 Pentene	$\text{CCl}_3\text{CO}_2\text{Na}$ CHCl_3		1,1-Dichloro-2,2-dimethylcyclopropane	Trace	
		KOC_4H_9 , t	2,2'-Bis(1,1-dichloro)cyclopropane	70	66
			1,1-Dichloro-2-vinylcyclopropane	—	84
			1,1-Dichloro 2- π -propylcyclopropane	—	
		KOC_4H_9 , t	<i>cis</i> 1,1-Dichloro-2-methyl-3-ethylcyclopropane	—	84

Note References 130 to 140 are on p. 90.

* The reactants were heated at reflux.

TABLE I—Continued
REACTIONS OF DICHLOROCARBENE WITH ALKENES, ALKYNES, AND CYCLOALKENES

Carbene Acceptor	Carbene Precursor	Base	Product(s)	Yield, %	Refs.
2-Methyl-1-butene	CHCl_3	$\text{KOC}_4\text{H}_9\text{-}t$	1,1-Dichloro-2-methyl-2-ethylcyclopropane	—	84
2-Methyl-2-butene	CHCl_3	$\text{KOC}_4\text{H}_9\text{-}t$	1,1-Dichloro-2,2,3-trimethylcyclopropane	66	8, 84
	$(\text{CCl}_3)_2\text{CO}$	NaOCH_3	1,1-Dichloro-2,2,3-trimethylcyclopropane	23	64
2-Methyl-1,3-butadiene	CHCl_3	$\text{KOC}_4\text{H}_9\text{-}t$	1,1,1,3,3,3-Hexachloro-2-propanol	—	—
2-Methyl-1-buten-3-yne	CHCl_3	$\text{KOC}_4\text{H}_9\text{-}t$	1,1-Dichloro-2-methyl-2-vinylcyclopropane	37	91, 86 92
			1,1-Dichloro-2-methyl-2-ethynylcyclopropane	65	95
Cyclopentadiene	CHCl_3		Chlorobenzene	23	130
1-Hexeno	CHCl_3	$\text{KOC}_4\text{H}_9\text{-}t$	1,1-Dichloro-2- <i>n</i> -butylcyclopropane	—	84
	CHCl_3	$\text{KOC}(\text{CH}_3)_2\text{C}_2\text{H}_5$	1,1-Dichloro-2- <i>n</i> -butylcyclopropane	16	8
1,5-Hexadiene	$\text{CCl}_3\text{CO}_2\text{Na}$	*	1,1-Dichloro-2-[butenyl-3]cyclopropane	23	66
2,3-Dimethyl-2-butene	CHCl_3	$\text{KOC}_4\text{H}_9\text{-}t$	1,1-Dichloro-2,2,3,3-tetramethylcyclopropane	—	84
	$\text{CCl}_3\text{CO}_2\text{Na}$	*	1,1-Dichloro-2,2,3,3-tetramethylcyclopropane	87	66
	CCl_4	†	1,1-Dichloro-2,2,3,3-tetramethylcyclopropane	—	131

2,3-Dimethyl-1,3-butadiene	CHCl_3	KOC_4H_9	—	92
2-Methyl-1-penten-3-yne	$\text{CCl}_3\text{CO}_2\text{Na}$	*	20	94
Cyclohexene	CBr_2Cl_2	$\pi \text{C}_4\text{H}_9\text{Li}$ NaOCH_3	91	9
	$\text{CCl}_3\text{CO}_2\text{C}_2\text{H}_5$	†	79-88	13
	$\text{C}_6\text{H}_5\text{HgCCl}_3$	CH_3Li	88	13a
	CCl_3I	CH_3Li	71	9
	CBrCl_3	*	67	9
	$\text{CCl}_3\text{CO}_2\text{Na}$	†	65	12, 68
	$\text{Cl}_2\text{SiCCl}_3$	KOC_4H_9 NaOCH_3	60	70
	CHCl_3	$\pi \text{C}_4\text{H}_9\text{Li}$	59	8, 84
	CCl_4	$\text{KCH}(\text{C}_6\text{H}_5)_2$	50	11, 64
	CHCl_3	$\pi \text{C}_4\text{H}_9\text{Li}$	50	9
	CCl_4	$\text{KCH}(\text{C}_6\text{H}_5)_2$	38	119
	CHCl_3	$\pi \text{C}_4\text{H}_9\text{Li}$	26	132
	CBrCl_3	$\text{KCH}(\text{C}_6\text{H}_5)_2$	19	83
	CHCl_3	$\text{KCH}(\text{C}_6\text{H}_5)_2$	17	132
	CCl_4	CH_3Li	15	132
Cyclohexene and $\text{CCl}_3\text{CO}_2^-$	$\text{CCl}_3\text{CO}_2\text{Ag}$	*	8	9
			10	68, 69
2-Methyl-2-hexen-4-yne	$\text{CCl}_3\text{CO}_2\text{Na}$	•	Major product 20	94
		Uncharacterized		
		Trichloroacetate anhydride		

Note References 130 to 140 are on p 90

* The reactants were heated at reflux.

† Electrophilic in acetone at -20° .

‡ The reactants were heated under reflux in benzene.

§ The reactants were heated at 250° .

TABLE I—Continued
REACTIONS OF DICHLOROCARBENE WITH ALKENES, ALKYNES, AND CYCLOALKENES


Carbene Acceptor	Carbene Precursor	Base	Product(s)	Yield, %	Refs.
3-Ethyl-2-penten-4-yne	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	1,1-Dichloro-2-ethyl-2-ethynyl-3-methylcyclopropane	40	95
1-Ethynylcyclopentene	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	1-Ethynyl-6,6-dichlorobicyclo[3.1.0]hexane	35	95
1-Methylcyclohexene	—	—	1-Methyl-7,7-dichlorobicyclo[4.1.0]heptane	—	133
Cycloheptatriene	CHCl ₃	NaOCH ₃	8,8-Dichlorobicyclo[5.1.0]octa-3,5-diene	20	130
	CCl ₃ CO ₂ Na	*	8,8-Dichlorobicyclo[5.1.0]octa-3,5-diene	46	12, 66
1-Octene	—	—	1,1-Dichloro-2-hexylcyclopropane	—	124
4-Vinylcyclohexene	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	Unidentified	—	8
β -Pinene	CHCl ₃	KOC ₄ H ₉ - <i>t</i> + <i>t</i> -C ₄ H ₉ OH	Unidentified	50	8
Ethylbenzene	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	None	—	86
Styrene	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	1,1-Dichloro-2-phenylcyclopropane	76	134
Phenylacetylene	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	None	—	86
1-Ethynylcyclohexene	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	1-Ethynyl-6,6-dichlorobicyclo[4.1.0]heptane	45	95
Cyclooctatetraene	CHCl ₃	KOC ₄ H ₉ - <i>t</i>	9,9-Dichlorobicyclo[6.1.0]nona-2,4,6-triene	—	135

Di- α -propylacetylene	$\text{CCl}_3\text{CO}_2\text{C}_2\text{H}_5$	NaOCH_3 ^a	Di- α propyl cyclopropenone	5	96
1-Dodecene	$\text{CCl}_3\text{CO}_2\text{Na}$	—	1,1 Dichloro 2-decyl cyclopropane	—	96
1-Cyclohexylcyclohexene	—	—	1-Cyclohexyl-7,7 dichlorobicyclo[4.1.0]heptane	—	124 133
1-Phenylcyclohexene	—	—	1-Phenyl-7,7 dichlorobicyclo[4.1.0]heptane	—	133
Diphenylacetylene	CHCl_3	KOC_4H_9 ^t	Diphenylcyclopropenone	24	98, 97
1- α Naphthylcyclohexene	—	—	1- α -Naphthyl 7,7- dichlorobicyclo[4.1.0]heptane	—	133
1 Octadecene	—	—	1,1 Dichloro-2- hexadecylcyclopropane	—	124

Note References 130 to 140 are on p 90.

^a The reactants were heated at reflux.

|| The product was obtained as the hydrochloride after hydrolysis of the adduct

Cyclohexene	$C_6H_5HgCBr_3$ $CHBr_3$	^a KOC_4H_9-4	7,7-Dibromobicyclo[4.1.0]heptane 7,7-Dibromobicyclo[4.1.0]heptane	88 75	13a 8, 14 84
1,4-Cyclohexadiene	$CBBr_4$ $CHBr_3$	LiC_4H_9-n KOC_4H_9-4	7,7-Dibromobicyclo[4.1.0]heptane 7,7-Dibromobicyclo[4.1.0]-3-heptene	11 70	9 136, 137, 138
				1	
Cycloheptene	$CHBr_3$	KOC_4H_9-4	8,8-Dibromobicyclo[5.1.0]octane	—	123
Cyclooctene	$CHBr_3$	KOC_4H_9-4	9,9-Dibromobicyclo[6.1.0]nonane	33	121, 122, 123 122
1,5-Cyclooctadiene	$CHBr_3$	KOC_4H_9-4	9,9,10,10-Tetrabromobicyclo[7.1.0.0.1.5]decane	34	135 95
Cyclooctatetraene	$CHBr_3$	KOC_4H_9-4	9,9-Dibromobicyclo[6.1.0]-4 nonene	—	134, 14, 122 86, 98
1-Ethynylcyclohexene	$CHBr_3$	KOC_4H_9-4	9,9-Dibromobicyclo[6.1.0]nona-2,4,6-triene	—	123
Styrene	$CHBr_3$	KOC_4H_9-4	1-Ethynyl-6,6-dibromobicyclo[4.1.0]heptane	50	134
Phenylacetylene	$CHBr_3$	KOC_4H_9-4	1,1-Dibromo-2-phenylcyclopropane	72	14 14
Cyclononene	$CHBr_3$	KOC_4H_9-4	Unidentified	—	
2-Phenyl-1-propene	$CHBr_3$	KOC_4H_9-4	10,10-Dibromobicyclo[7.1.0]decane	—	
3-Phenyl-1-propene	$CHBr_3$	KOC_4H_9-4	1,1-Dibromo-2-methyl-2-phenylcyclopropane	81	
1-(p-Methoxyphenyl)-1-propene	$CHBr_3$	KOC_4H_9-4	1,1-Dibromo-2-benzylcyclopropane	13	
1-Phenylcyclohexene	—	—	1,1-Dibromo-2-methyl-3-(p-methoxyphenyl)cyclopropane 1-Phenyl-7,7-dibromobicyclo[4.1.0]heptane	47 —	

Notes. References 130 to 140 are on p 90

^a The reactants were heated under reflux in benzene.

TABLE II—Continued

REACTIONS OF DIHOMO- AND DIFLUORO-CARBENES WITH ALKENES, ALKYNES, AND CYCLOALKENES				
Carbene Acceptor	Carbene Precursor	Base	Product(s)	Yield, %
1,9-Cyclotetradecadiene	CHBr_3	$\text{KOC}_4\text{H}_9\text{-}t$	15, 15, 16, 16-Tetrabromotricyclo[13.1.0.0 ^{1,14}]hexadecane	22
Diphenylacetylene	CHBr_3	$\text{KOC}_4\text{H}_9\text{-}t$	Diphenylcyclopropenone†	28
	CHCl_2F	$\text{KOC}_4\text{H}_9\text{-}t$	7-Chloro-7-fluorobicyclo[4.1.0]heptane	24
Cyclohexene	$(\text{CH}_3)_3\text{SnCF}_3$	†	Perfluorocyclopropane	95
	KCF_3BF_3	§	Tetrafluoroethylene, fluoroform	---
Tetrafluoroethylene	KCF_3BF_3		Tetrafluoroethylene	89
	KCF_3BF_3		Perfluorocyclobutane, perfluorocyclopropane	Trace
Cyclohexene	$(\text{CH}_3)_3\text{SnCF}_3$	†	Perfluorocyclobutane	80
	CHClF_2	$\text{KOC}_4\text{H}_9\text{-}t$	Phenoldefinis	100
Cyclohexene	$\text{CF}_3\text{ClO}_2\text{Na}$	†	Perfluorocyclopropane	Trace
	$\text{CF}_3\text{ClO}_2\text{Na}$	†	Perfluorocyclobutane	---
Cyclohexene	$\text{CF}_3\text{ClO}_2\text{Na}$	†	Unidentified	57
	$\text{CF}_3\text{ClO}_2\text{Na}$	†	7,7-Difluorobicyclo[4.1.0]heptane	65
			Carbon dioxide	60-65

Note: References 130 to 140 are on p. 90.

† The product was obtained as the hydrochloride after hydrolysis of the adduct.

‡ Pyrolysis.

§ Pyrolysis at 300° in vacuum.

|| Pyrolysis at 450° in vacuum.

TABLE III
REACTIONS OF DIHALOCARBENES WITH DOUBLE BONDS IN AROMATIC AND HETEROCYCLIC COMPOUNDS

Carbene Acceptor	Carbene Precursor	Base	Product(s)	Yield, %	R _f fo.
Pyrrole	CHCl ₃	Pyrrylsodium	3-Chloropyrindine*	4	59
	CHCl ₃	Pyrrylpotassium	3-Chloropyrindine	13	59
	CHCl ₃	Pyrryllithium	3 Chloropyrindine	7	59, 37
2 Methylpyrrole	CHCl ₃	2-Methyl- pyrrylpotassium	2-Methyl-3-chloropyrindine	-	37
2,3-Dihydropyran	CCl ₃ CO ₂ C ₂ H ₅	NaOCH ₃	7,7-Dichloro-2-oxabicyclo[4.1.0]heptane	75	119
Benzene	CHCl ₃	KOC ₂ H ₅ †	None	-	60, 99
2,5-Dimethylpyrrole	CHCl ₃	NaOC ₂ H ₅	3 Chlorolutidine*	-	35
Anisole	CHCl ₃	KOC ₂ H ₅ †	None	-	86
Indene	CHCl ₃	Indenylsodium	2-Chloronaphthalene	10	101
			5 Chloroazulene	Trace	
2-Bromonaphthalene	CHCl ₃	KOC ₂ H ₅ †	1,1-Dichlorocycloprop[α]indene	65	50
2 Chloronaphthalene	CHCl ₃	KOC ₂ H ₅ †	1,1-Dichlorocycloprop[α]indene	33	57
2-Methylindole	CHCl ₃	KOC ₂ H ₅ †	Unidentified naphthalenic product†	2	89
Skatole	CHCl ₃	NaOC ₂ H ₅	1,2-Dichloronaphthalene†	5	89
2H-1-Benzopyran	CHCl ₃	NaOC ₂ H ₅	3 Chloroquinoline*	-	33
	CCl ₃ CO ₂ C ₂ H ₅	NaOCH ₃	3-Chlorolepidine*	-	33
4H-1-Benzopyran	CCl ₃ CO ₂ Na		1,1-Dichlorocyclopropa[c][1]benzopyran	92	90a
4H-1-Benzopyran	CCl ₃ CO ₂ C ₂ H ₅	NaOCH ₃	1,1-Dichlorocyclopropa[c][1]benzopyran	24	90a
4H-1-Benzothiohypan	CCl ₃ CO ₂ C ₂ H ₅	NaOCH ₃	1,1-Dichlorocyclopropa[b][1]benzopyran	83	90a
			1,1-Dichlorocyclopropa[b][1]benzothiohypan	82	90
2-Methylindene	CCl ₃ CO ₂ Na	†	1,1-Dichlorocyclopropa[b][1]benzothiohypan	24	90
	CHCl ₃	KOC ₂ H ₅ †	2-Chloro-3-methylnaphthalene†	37	89

Note. References 130 to 140 are on p. 90.

* The reaction was run in the presence of ethanol

† The reactants were heated at reflux in diethylene glycol dimethyl ether

† The product was obtained after treatment with water.

TABLE III—Continued
REACTIONS OF DIHALOCARBENES WITH DOUBLE BONDS IN AROMATIC AND HETEROCYCLIC COMPOUNDS

Carbonyl Acceptor	Carbonyl Precursor	Base	Product(s)	Yield, %	Refs.
1-Methoxynaphthalene	$\text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$	NaOCH_3	7-Chloro-2,3-benzotropono Methyl chloride	11	100
2-Methoxynaphthalene	$\text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$	NaOCH_3	7-Chloro-4,5-benzotropono	13	100
1,2,3,4-Tetrahydrocarbazole	CHCl_3	NaOC_2H_5	Unidentified product, $\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{N}$	—	34
2-Carboethoxyindene	CHCl_3	KOC_4H_9	Unidentified product	—	89
9-Methoxyphenanthrene	$\text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5$	NaOCH_3	1,1-Dichloro-1a-methoxy-11H-cyclopropa[1]phenanthrene	52	100
Indene	CHBr_2Cl	KOC_4H_9	2-Chloronaphthalene	35	57
Pyrrole	CHBr_3	Pyrrolithium	2-Bromonaphthalene	35	59
	CHBr_3	Pyrrolsodium	3-Bromopyridine	9	59
	CHBr_3	Pyrrolpotassium	3-Bromopyridine*	3	59
Benzene	CHBr_3	KOC_4H_9	4-Bromopyridine	—	104
2,4-Dimethylpyrrole	CHBr_3	NaOC_2H_5	None	—	60
			2,5-Dimethyl-3-bromopyridine*	—	35
2,5-Dimethylpyrrole	CHBr_3	NaOC_2H_5	2,4-Dimethyl-5-bromopyridine	—	35
Indene	CHBr_3	KOC_4H_9	3-Bromolindene	—	35
2-Methylindole	CHBr_3	KOC_4H_9	2-Bromonaphthalene†	52	50
Skatole	CHBr_3	NaOC_2H_5	3-Bromoquinoline*	—	33
1-Methylindene	CHBr_3	NaOC_2H_5	3-Bromolindene*	—	33
2-Methyl-5-phenylpyrrole	CHBr_3	KOC_4H_9	1-Methyl-2-bromonaphthalene	44	50
Indene	CHI_3	KOC_4H_9	Unidentified pyridine base*	Trace	35
			None	—	33

Note: References 130 to 140 are on p. 90.

* The reaction was run in the presence of ethanol.

† The product was obtained after treatment with water.

TABLE IV
REACTIONS OF DIHALOCARBENES WITH MISCELLANEOUS UNSATURATED COMPOUNDS

Carbene Acceptor	Carbene Precursor	Base	Product(s)	Yield, %	Refs.
Allyl chloride	$\text{CCl}_2\text{CO}_2\text{Na}$	KOC_2H_5 , a	1,1-Dichloro-2-chloromethylcyclopropane	60	66
Ethyl vinyl ether	CHCl_3	NaOCH_3	1,1-Dichloro-2-ethoxycyclopropane	—	84
Divinyl ether	$\text{CCl}_2\text{CO}_2\text{C}_2\text{H}_5$	NaOCH_3	Bis-(2,2-dichlorocyclopropyl) ether	16	139
Vinyl acetate	$\text{CCl}_2\text{CO}_2\text{Na}$	KOC_2H_5 , a	1,1,1-Trichloro-2-acetoxy- α -propane	10	68
Ketene dimethylacetal	CHCl_3	KOC_2H_5 , a	1,1-Dichloro-2,2-dimethoxycyclopropane	4	123
Hexachlorobutadiene	CHCl_3	KOC_2H_5 , a	None	—	89
Methylketene dimethylacetal	CHCl_3	KOC_2H_5 , a	1,1-Dichloro-2,2-dimethoxy-3-methylcyclopropane	52	128
Ketene diethylacetal	CHCl_3	KOC_2H_5 , a	1,1-Dichloro-2,2-diethoxycyclopropane	68	123
Dimethylketene dimethylacetal	CHCl_3	KOC_2H_5 , a	1,1-Dichloro-2,2-dimethoxy-3,3-dimethylcyclopropane	61	128
Ethylketene dimethylacetal	CHCl_3	KOC_2H_5 , a	1,1-Dichloro-2,2-dimethoxy-3-ethylcyclopropane	56	128
n-Propylketene dimethylacetal	CHCl_3	KOC_2H_5 , a	1,1-Dichloro-2,2-dimethoxy-3-n-propylcyclopropane	55	128
Diisobutyl ether	$\text{CCl}_2\text{CO}_2\text{C}_2\text{H}_5$	NaOCH_3	Bis-(2,2-dichloro-3,3-dimethylcyclopropyl) ether	20	139
2H-1-Benzothiofuran	CHBr_3	KOC_2H_5 , a	2-Dichloromethyl-2H-1-benzothiofuran	28	139
	$\text{CCl}_2\text{CO}_2\text{C}_2\text{H}_5$	NaOCH_3	4-Dichloromethyl-4H-1-benzothiofuran	22	90
	$\text{CCl}_2\text{CO}_2\text{Na}$	a	Undenitified diadduct, $\text{C}_{10}\text{H}_8\text{Cl}_2\text{S}$	9	
Phenylketene dimethylacetal	CHCl_3	KOC_2H_5 , a	2-Dichloromethyl-2H-1-benzothiofuran	15†	90
			Dimethyl t-butyl orthophenylpropionate	15	
			Methyl phenylpropionate	20	128
			Methyl phenylacetate	50	
Benzaldehyde	CHCl_3 (CCl_3) ₂ CO	NaOCH_3 NaOCH_3	2,2-Dichloro-1,3-diphenylethylbenzene	19	107
			2,2-Dichloro-1,3-diphenylethylbenzene	61	64

Note. References 130 to 140 are on p. 90.

^a The reactants were heated at reflux in diethylene glycol dimethyl ether.

† The yields of the products were estimated from nuclear magnetic resonance spectral data.

TABLE V
REACTIONS OF MONOHALOCARBENES

Carbene Acceptor	Carbene Precursor	Base	Product(s)	Yield, %	Refs.
2-Methylpropene	CH_3Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	1-Chloro-2,2-dimethylcyclopropane	44	83
	CH_2Cl_2	CH_3Li	1-Chloro-2,2-dimethylcyclopropane	50	83
<i>cis</i> -2-Butene	CH_2Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	1-Chloro- <i>cis</i> -2,3-dimethylcyclopropane (the <i>cis/trans</i> chlorino ratio was 1:5.5)	30	83
<i>trans</i> -2-Butene	CH_2Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	1-Chloro- <i>trans</i> -2,3-dimethylcyclopropane	40	83, 10
Pyrrole	CH_2Cl_2	CH_3Li	Pyridine	32	106
1,2-Dimethylpropenyl lithium	CH_2Cl_2	CH_3Li	1,3,3-Trimethylcyclopropene*	40-50	140
2-Methyl-1,2-butene	CH_2Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	1-Chloro-2,2,3-trimethylcyclopropane (the <i>cis/trans</i> ratio was 1:1.6)	50	83
1-Pentene	CH_2Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	1-Chloro-2- <i>n</i> -propylcyclopropane (the <i>cis/trans</i> ratio at -35° , 1:3.4)	10	83
	CH_2Cl_2	CH_3Li	1-Chloro-2- <i>n</i> -propylcyclopropane (the <i>cis/trans</i> ratio at 30° , 1:1.8)	25	83
Dihydropyran	CH_2Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	7-Chloro-2-oxabicyclo[4.1.0]heptano (the <i>exo/endo</i> ratio was 3.2:1)	28	119
2,3-Dimethyl-2-butene	CH_2Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	1-Chloro-2,2,3,4-tetramethylcyclopropane	67	83, 10

Cyclohexene	CH_2Cl_2	$n\text{-C}_4\text{H}_9\text{Li}$	7-Chlorobicyclo[4.1.0]heptano (the <i>exo/endo</i> ratio was 2.2:1)	31	10
	CH_2Cl_2	CH_3Li	7-Chlorobicyclo[4.1.0]heptano (the <i>exo/endo</i> ratio was 3.2:1)	48	83
Benzene	CH_2Cl_2	CH_3Li	Methylcycloheptatriene	20	99
	CH_3Cl_2		Ethylene	—	
Lithium phenoxide	CH_3Cl_2	KOC_4H_9 [†]	<i>t</i> -Butoxycycloheptatriene [†]	2	60
	CH_2Cl_2	CH_3Li	Tropone	0.2	103
			2-Methyl-3,5-cycloheptadienone	44	
Lithium <i>o</i> -cresyloxide	CH_2Cl_2	CH_3Li	Methyltropilium chloroplatinate [‡]	4	
			2,7-Dimethyl 3,5-cycloheptadienone	23	103
Indole			1,2-Dimethyltropilium chloride [‡]	3	
2,6-Di- <i>t</i> butylphenoxide	CH_2Cl_2	CH_3Li	Quinoline	13	106
Benzene	CH_2Cl_2	CH_3Li	2,7-Di- <i>t</i> -butyltropone	70	103
Pyroole	CH_2Br_2	KOC_4H_9 [†]	<i>t</i> -Butoxycycloheptatriene [†]	1	60
Benzene	CH_2I_2	NaOC_4H_9	Pyridine	Trace	59, 61
	CH_2I_2	KOC_4H_9 [†]	<i>t</i> -Butoxycycloheptatriene [†]	0.1	60

Note References 130 to 140 are on p. 90.

* The intermediate 2,3,3-trimethylcyclopropenyllithium was hydrolyzed to obtain the product listed.

† The product was isolated as the tropilium bromide after treatment with hydrogen bromide.

‡ The product was isolated after acidification.

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CHAPTER 3

FREE RADICAL ADDITIONS TO OLEFINS TO FORM CARBON-CARBON BONDS

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INTRODUCTION

Some of the most useful reactions in synthetic organic chemistry involve the addition of reagents across the double bonds of olefins. These reactions, which can occur by a variety of mechanisms involving electrophilic, nucleophilic, or radical intermediates, have been the subject of numerous mechanistic studies. Electrophilic additions involve polar reagents, and in general the direction of addition follows Markownikoff's rule. Nucleophilic additions require rather special and drastic conditions unless the olefin contains strong electron-withdrawing substituents. Radical reactions are very general in scope but are markedly influenced by light, oxygen, peroxides, and various inhibitors.

The direction of addition in the free radical reaction is commonly the opposite of that encountered in the electrophilic ionic (Markownikoff) additions. Hence these free radical additions have been referred to as

anti-Markownikoff, abnormal, or, more recently, Kharasch addition reactions. This chapter is concerned with the synthetic aspects of Kharasch addition reactions that result in the formation of a new carbon-carbon bond.

The discovery that certain compounds could add to olefins by a free radical chain reaction was made in the nineteen-thirties. The presently accepted mechanism of the anti-Markownikoff addition of hydrogen bromide and mercaptans was suggested by Kharasch in 1937,¹ and

TABLE I

Class	Products
Polyhalomethanes	Halogenated hydrocarbons
Aldehydes	Ketones
Alcohols	
Primary	Secondary alcohols
Secondary	Tertiary alcohols
Methanol	Primary alcohols
Amines	Amines alkylated on the α -carbon atom
Esters (and other acid derivatives)	α -Alkyl esters (and other acid derivatives)
Formate esters	Monocarboxylic esters
Ethers	Ethers alkylated on the α -carbon atom

independently by Waters² in the same year. The first examples of a simple addition reaction resulting in the formation of a new carbon-carbon bond were given in 1945 by Kharasch, who reported that carbon tetrachloride and chloroform reacted with 1-octene to form 1,1,1,3-tetrachlorononane and 1,1,1-trichlorononane, respectively.³

It had previously been noted that carbon tetrachloride had a marked effect in lowering the degree of polymerization of styrene, an observation explained quantitatively by Mayo in 1943 in terms of a chain transfer process.⁴ Also prior to the Kharasch publication, the addition of carbon tetrachloride to olefins to form products of low molecular weight had been observed independently by research groups at the du Pont and U.S. Rubber companies.⁵ Since this time, a number of other compounds have been found to add to olefins in a free radical chain reaction. In Table I, those classes of compounds which on addition to an alkene result

¹ Kharasch, Engelmann, and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

² Hey and Waters, *Chem. Rev.*, **21**, 168 (1937).

³ Kharasch, Jensen, and Urry, *Science*, **102**, 138 (1945).

⁴ Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943).

⁵ Walling, *Free Radicals in Solution*, p. 247, John Wiley and Sons, Inc., New York, 1957.

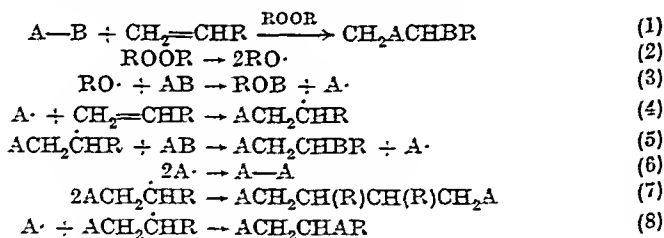
in the formation of a new carbon-carbon bond are listed along with the resulting addition products.

Although the majority of these Kharasch additions have been performed with alkenes as the unsaturated species, many other unsaturated compounds, e.g., vinyl acetate, maleate esters, allyl halides, have been used with success and have led to the formation of di- or poly-functional addition products. Additions to simple olefins and to olefins containing other functional groups are included in the Tabular Survey.

MECHANISM

Characteristics of Radical Chain Reactions

Because the addition reactions discussed in this chapter are typical radical chain reactions, some comments on such processes are in order. The over-all reaction in which a molecule $A-B$ is added across a double bond in the presence, for example, of a peroxidic initiator actually occurs through a complex sequence of steps involving transient free radicals as intermediates. These steps may be indicated as follows.



In such a scheme steps (2) and (3) represent chain initiation, (6) to (8) chain termination, and (4) and (5) chain propagation.

The reactions represented by equations 4 and 5 are the important steps in determining the products since the radical $A\cdot$ consumed in (4) in an addition reaction is regenerated in (5), a radical displacement reaction, and many (often hundreds or thousands) of such cycles may occur for every radical introduced into the system. In contrast, since chain termination steps destroy radicals, no more termination products are produced than chains are started; they contribute little to the reaction, and the over-all stoichiometry of the process (in the absence of side reactions which involve alternative chain propagation steps) is essentially that of reaction 1. On the other hand, the *over-all reaction rate* and the *kinetic chain length* (or molecules of product produced per molecule of initiator starting chains) which essentially determine the *yield* under a given set of experimental conditions depend on each of the three processes of initiation, propagation,

and termination. The rate of initiation of chains can in general be controlled by suitable choice of initiator, temperature, and other experimental conditions. The rate of chain termination is subject to no such direct control and imposes a very serious limitation on the scope of chain processes. Bimolecular reactions between radicals such as (6) to (8) almost invariably have very high rate constants ($\sim 10^7$ l/mole/sec.), with the consequence that the time interval between the initiation and termination of a chain is only of the order of a second. If a large number of chain propagation steps are to be interposed into such a short time interval, it is evident first that they must be very rapid, low activation energy processes and, second, that small changes in structure of the addend AB or olefin may have large effects on over-all rates and yields.

The effect of changes of structure on reactivity in radical reactions can be treated quite successfully in terms of resonance, steric, and polar phenomena (pp. 95-99). When due allowance is made for the side reactions discussed below, these factors permit a satisfactory semiquantitative picture of radical addition reactions even though relatively few detailed kinetic studies of such systems have been published.

Lewis and Mayo have investigated the effect of olefin/addend ratio on yields in a number of halomethane additions with results which appear to be quite general.⁸ At low olefin/addend ratios, reaction 4 becomes the slow step in propagation, radical A \cdot accumulates in the system, and chain termination occurs through (6), with the kinetic consequence that the over-all reaction is first-order in olefin. At high olefin/addend ratios, (5) is the slow propagation step, termination occurs through (7), and the over-all reaction is first-order in addend. At intermediate ratios, termination may involve both (6) and (7) and also (8), but the general result is a rather pronounced maximum in rate (or yield with a given amount of initiator) at some particular olefin/addend ratio. Some typical yield curves are shown in Fig. 1 and support this conclusion. They also illustrate the profound sensitivity of these addition reactions to small changes in structure to which we now turn our attention.

Structure and Reactivity

The over-all addition reaction 1, where A \cdot is a hydrocarbon radical, is in general exothermic by about 20 kcal/mole. However, if both propagation steps (4) and (5) are to be rapid, low activation energy processes, this energy must be suitably divided between the two, or in any case the balance should not be so poor that one is significantly endothermic. The manner in which this division occurs is determined primarily by the

⁸ Lewis and Mayo, *J. Am. Chem. Soc.*, **76**, 457 (1954).

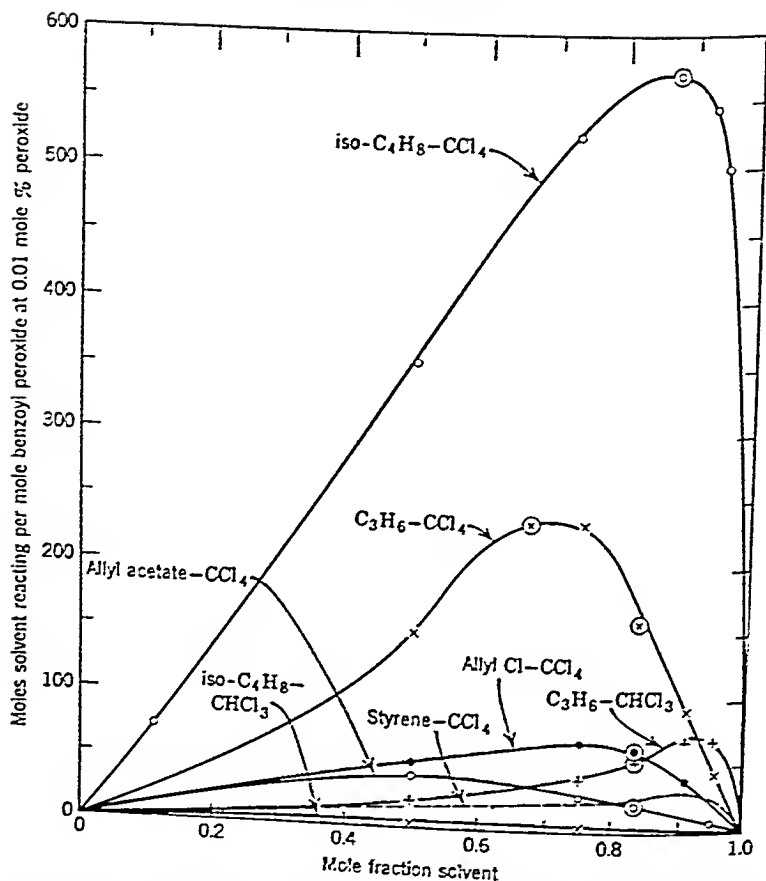


FIG. 1. Variation in yield with solvent/olefin ratio in radical addition of halomethanes to olefins. From C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957, p. 269.

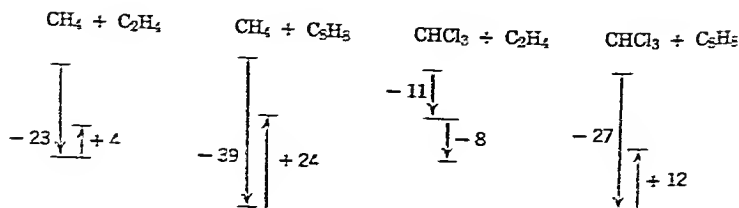


FIG. 2. Energetics of addition of CH₄ and CHCl₃ to ethylene and styrene, in kilocalories per mole. First arrow for reaction (4), second for reaction (5). Data assume $\Delta H_{(\text{over-211})} = -19$ kcal. for ethylene additions and -15 kcal. for styrene.

effective resonance energies of the radicals $A\cdot$ and $R\cdot$ involved in the two steps*. This resonance energy can be deduced from bond dissociation energy data, and typical values appear in Table II; the methyl radical, $CH_3\cdot$, is taken as a standard for comparison. Since in reaction (4) the resonance energy of $A\cdot$ is lost and that of $R\cdot$ is gained, a highly stabilized $A\cdot$ radical will decrease the exothermicity of the process, while substituents on the olefin leading to a highly stabilized radical $R\cdot$ will increase the exothermicity. In reaction (5) the resonance energy of $ACH_2\dot{C}HR$ is lost while that of $A\cdot$ is gained, and the opposite situation results. As examples,

TABLE II
BOND DISSOCIATION ENERGIES AND RESONANCE ENERGIES
OF FREE RADICALS

Bond	$\Delta H_0 D(R-H),$ kcal/mole	Resonance Energy of Radical, kcal/mole
H—CH ₃	102	0
H—C ₂ H ₅	98	4
H—CH ₂ CH ₂ CH ₃	100	2
H—CH(CH ₃) ₂	94	8
H—C(CH ₃) ₃	90	12
H—CH ₂ CH=CH ₂	77	25
H—CH ₂ C ₆ H ₅	77.5	24.5
H—C(CH ₃) ₂ CO ₂ CH ₃	(75) ^a	27
H—CCl ₃	90	12
Cl—CCl ₂	68	12
Br—CCl ₂	49	12
I—CCl ₂	(39) ^a	12

* This value has a larger uncertainty than those not in parentheses. See reference 3, pp. 47-49.

Fig. 2 illustrates the calculated energetics of addition of methane and chloroform (as CH_3-H and CCl_3-H) to ethylene and to styrene. Here $\cdot CCl_3$ and the radical $R\cdot$ from styrene are stabilized by approximately 12 and 24 kcal/mole, respectively. Replacing $CH_3\cdot$ by $CCl_3\cdot$ decreases the exothermicity of reaction (4) and increases that of (5). On the other hand, replacing ethylene by styrene increases the exothermicity of (4) and decreases that of (5). Only in the chloroform-ethylene system are both steps exothermic, and this is also the only one of the four reactions which has been observed as a long-chain process giving a simple 1,1 adduct. Similar approximate calculations can be made for other systems by correcting the basic energetics of the methane-ethylene reaction by the resonance stabilization values given in Table II.

* Resonance stabilization of the double bond also plays a minor role in the division but is not taken into account in this brief discussion.

In a series of addends $A-B$ in which the carbon radical $A\cdot$ is held constant and B is changed, reactivity generally increases in the sequence $H < Cl < Br < I$. Thus CCl_3-Br undergoes addition more readily than CCl_3-Cl , and CF_3-I more readily than CF_3-Br . The differentiation between $Cl-$ and $H-$ is less clear-cut and depends to some extent on the particular system involved. Thus chloroform is usually less reactive than carbon tetrachloride and adds as CCl_3-H . Bromoform is more reactive and adds as $CHBr_2-Br$. On the other hand, aldehydes add as $RCO-H$, while acid chlorides fail to give a comparable addition as $RCO-Cl$. No displacement involving fluorine is known, and, although displacements involving other atoms attached to carbon have been observed, they do not in general lead to carbon-carbon bond formation and accordingly are outside the scope of this chapter.

Although it is advantageous for the radical reactions to be exothermic, this is not solely sufficient to provide for fast radical chains. Even strongly exothermic processes may have significant activation energies, and small differences in activation energies (or in pre-exponential factors) may lead to large differences in rate. These more subtle effects of structure have been studied in detail, chiefly by the use of competitive reactions, and can be discussed in terms of steric and polar factors.

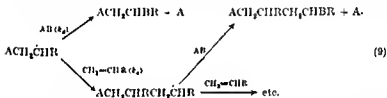
Steric hindrance affects radical reactions, particularly in the addition step (4). Thus non-terminal olefins generally undergo addition reactions less readily than terminal olefins and give lower yields of the desired products. In fact, the usual direction of addition in radical reactions, in which the radical $A\cdot$ adds to the less-substituted end of the double bond, is probably largely a steric effect, although it is also aided by the greater resonance stabilization of the resulting radical. Steric hindrance in the displacement step (5) seems to be less important and, in fact, is not well established.

Another factor which plays a very important role in the rates of both radical displacements and additions appears to be polar in nature: radicals with strong electron-withdrawing groups show enhanced reactivity with substrates bearing electron-supplying groups, and vice versa. The nature of this polar effect has received considerable discussion and appears to vary from a simple dipolar interaction to, in extreme cases, the lowering of the energy of the transition state by contributions from charge transfer structures. We may note that radicals with electron-withdrawing groups that have corresponding negative ions of reasonable stability add with particular facility to olefins of high electron availability, while radicals with stable corresponding carbonium ions add well to olefins bearing electron-withdrawing groups. Thus polyhalomethanes react readily with hydrocarbons, vinyl ethers, etc., while aldehydes and alcohols

(which add as $RCH(OH)-H$) give particularly good yields of adducts with perfluoroolefins and α,β unsaturated carbonyl compounds such as maleate esters. The reality of these polar effects has been amply demonstrated by the study of competitive reactions, and the effects appear to be as important as the other factors mentioned above in determining the success or failure of a given reaction.*

Telomer Formation

The radical addition described by the reaction sequence (2-8) may be subject to competing processes which interfere with the desired chain. The most important is polymerization. Actually, reaction (5) is always in competition with addition of the olefin-derived radical to another molecule of olefin. The result is that, besides the simple addition product,



ACH_2CHBR , a series of higher products, $\text{A}(\text{CH}_2\text{CHR})_n\text{CH}_2\text{CHBR}$, may be produced as well. These materials, known as telomers, are usually undesired by-products because they have rather complex branched structures. However, in the case of ethylene and tetrafluoroethylene, telomerization provides a powerful synthetic method for the preparation of long-chain molecules $\text{A}(\text{CH}_2\text{CH}_2)_n\text{B}$ and $\text{A}(\text{CF}_2\text{CF}_2)_n\text{B}$.

The importance of telomer formation can be assessed quantitatively in terms of the transfer constant C , the ratio of the rate constants for reaction of an olefin derived radical $R\cdot$ with AB and with another molecule of olefin. A simple kinetic analysis shows that, in reaction (9),

$$\frac{\text{mole fraction 1:1 product}}{\text{mole fraction telomers}} = \frac{k_d[\text{AB}]}{k_a[\text{olefin}]} = C_1 \frac{[\text{AB}]}{[\text{olefin}]} \quad (10)$$

where C_1 is the first transfer constant involving the reaction of $R\cdot$ containing just one olefin unit. In the same manner, the expression may be generalized

$$\frac{\text{mole fraction } N:1 \text{ product}}{\text{mole fraction higher products}} = C_N \frac{[\text{AB}]}{[\text{olefin}]} \quad (11)$$

* For a further discussion of these effects see reference 2, pp. 132-140

The resulting distribution functions have been worked out so that the entire product distribution can be calculated for systems in which the transfer constants are known.*

With $C > 1$, high yields of 1:1 products can be obtained with a small excess of AB. In principle, good yields can also be obtained in systems where $C \ll 1$ by working at very high ratios of $[AB]/[\text{olefin}]$, or by adding

TABLE III
VARIATION OF TRANSFER CONSTANTS FOR POLYHALOMETHANES
WITH CHAIN LENGTH⁷

System	C_1	C_2	C_n
Ethylene- CCl_4 (70°)	0.08	1.9	3.2 ^a
Propylene- CCl_4 (100°)	1.3		5-10
Propylene- CHCl_3 (100°)	0.11 ± 0.01	0.55 ± 0.03	1.03 ± 0.05
Isobutylene- CCl_4 (100°)	1.4 ± 0.4		17 ± 3
Allyl chloride- CCl_4 (100°)	$0.01 - 0.02$	0.10 ± 0.05	0.48 ± 0.03
Allyl acetate- CCl_4 (100°)	0.01 ± 0.01	0.5 ± 0.2	2.0 ± 1.0
Styrene- CCl_4 (76°)	0.0006	0.0025	0.0115^b

^a This is the value for C_3 .

^b The value for C_3 is 0.004.

the olefin slowly during the reaction, although kinetic chains may be short under these conditions, thus requiring a relatively large amount of initiator. Since small transfer constants generally increase with temperature, better yields of 1:1 product may also be obtained at higher temperatures.

Optimizing the yield of a telomer containing a particular number of olefin units is a more complicated matter. The yield of any particular telomer is dependent on the addend/olefin ratio and passes through a maximum value at a particular addend/olefin ratio. The situation is helped somewhat by the fact that transfer constants frequently increase significantly until $n = 3$ or 4, so that quite good yields of 2:1 or 3:1 products can be obtained. Some typical values are listed in Table III.

Transfer constants vary with structure in the manner suggested by the previous discussion. In the addend A—B, they increase with changes in B from $\text{H} < \text{Cl} < \text{Br} < \text{I}$, and with substituents in A that increase its resonance stabilization, since all these changes increase the rate of the displacement reaction. Thus bromotrichloromethane gives good yields of 1:1 products in reactions with equimolecular quantities of most olefins, while carbon tetrachloride must be used at high carbon tetrachloride/olefin ratios. Polyhalomethanes with less than three halogens generally give

* See Ref. 5, chap. 6.

⁷ Ref. 5, p. 257.

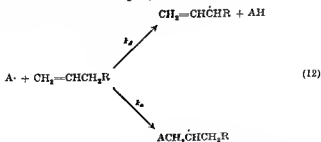
low yields of 1:1 products unless the methanes are further activated by nitrile, carbonyl, or similar groups.

The situation with olefins is slightly more complicated. Substituents stabilizing $R\cdot$ also increase olefin reactivity, so the tendency to add another olefin does not change greatly with structure. On the other hand, resonance stabilization of $R\cdot$ decreases the rate of the displacement reaction, so telomer formation is favored. Thus ethylene, vinyl acetate, and other olefins which polymerize well alone but react via highly reactive, unstabilized radicals give 1:1 products in many systems. In contrast, styrene and methyl acrylate usually give only telomers of high molecular weight. Non-terminal olefins, in which polymerization is retarded by steric hindrance, show little tendency to form telomeric products, although the desired 1:1 addition may not occur in high yield.

Finally, polar effects may again play a decisive role in the competition of reaction (9), as well as in the rate of the over-all addition reaction. As examples, perfluoroolefins have high transfer constants with alcohols and give good yields of 1:1 products with alcohols, in contrast to non-fluorinated olefins such as ethylene.

Allylic Attack

A second complication in radical addition processes arises from the possibility of competition between the desired addition (4) and displacement reactions between the radical $A\cdot$ and the olefin. Here attack upon allylic hydrogen atoms is particularly likely because of the high resonance stabilization of the resulting allylic radical,



and the importance of the reaction depends obviously on the ratio of rate constants k_d/k_a in equation 12. The role of such a side reaction in polymerization was first pointed out by Bartlett and Altschul,⁸ and its importance in radical additions by Israelashvili and Shabatay.²

⁸ Bartlett and Altschul, *J. Am. Chem. Soc.*, **67**, 828 (1945).

² Israelashvili and Shabatay, *J. Chem. Soc.*, 1951, 3261.

The few available estimates of the values of k_d/k_a ratios give an idea of the amount of side reaction to be expected. For the reaction of methyl radicals with isobutylene at 65°, $k_d/k_a = 0.06$, and increases to 0.95 and 0.7 for *cis*- and *trans*-2-butene, presumably because of the decreased rate of addition to a non-terminal double bond.¹⁰ When A· is a more highly resonance-stabilized radical, the amount of allylic attack is decreased. The situation with the CCl₃· radical has been studied in some detail.^{11,12} For 1-hexadecene, k_d/k_a is 0.018, while for cyclohexene it is approximately 0.5. The data in Table IV illustrate the influence of some structural

TABLE IV

RELATIVE AMOUNTS OF HYDROGEN ABSTRACTION AND ADDITION
BY THE TRICHLOROMETHYL RADICAL WITH VARIOUS OLEFINS¹²

Olefin	Temperature, °C.	k_d/k_a
<i>cis</i> -2-Butene	99.0	0.029
<i>trans</i> -2-Butene	99.0	0.038
2-Pentene	77.8	0.18
Cyclopentene	77.8	0.18
	40.0	0.54
4-Methyl-2-pentene	77.8	0.81
	40.0	0.60
Cyclohexene	77.8	0.83
	40.0	0.54
3-Heptene	77.8	0.29
	40.0	0.20
Cycloheptene	77.8	0.18
	40.0	0.12
1-Octene	77.8	0.023
1-Decene	77.8	0.023

features of the olefin on the amount of allylic attack. Terminal olefins, with double bonds that are very reactive toward addition, suffer comparatively little allylic attack in comparison to non-terminal olefins. Furthermore, non-terminal olefins with very reactive allylic hydrogen atoms, such as the tertiary allylic hydrogen atom in 4-methyl-2-pentene and the ring hydrogen atoms in cyclohexene, suffer a considerable amount of allylic attack.

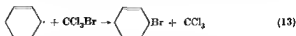
Allylic attack is a complication in addition reactions, not only because it introduces a competing side reaction, but also because it may lead to the termination of kinetic chains with a resulting reduction of over-all

¹⁰ Buckley, Leavitt, and Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956).

¹¹ Kooyman, *Discussions Faraday Soc.*, **10**, 163 (1951).

¹² Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

product yield. Since the resulting allylic radical is a highly resonance-stabilized species, it may fail to react with the addend A—B and instead accumulate in the system until it disappears by bimolecular coupling or disproportionation reactions. This difficulty shows up very plainly in addition reactions to cyclohexene. Carbon tetrachloride gives only low yields of any product, while bromotrichloromethane gives a rapid reaction with long kinetic chains. Here the allylic radicals re-enter the chain by the sequence



and, from the value of k_d/k_s given, about a third of the olefin that reacts would be converted to 3-bromocyclohexene and about two-thirds to the addition product 1-trichloromethyl-2-bromocyclohexane.

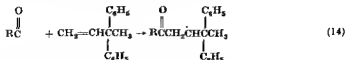
More detailed discussions of the kinetic significance of allylic attack are available.^{8,11,13}

Rearrangements

The rearrangements that sometimes accompany radical additions may be classified in three types: 1,2 shifts, ring opening and closure, and a miscellaneous group. A more detailed discussion of radical rearrangements in general is given elsewhere.¹⁴

In radical processes 1,2 shifts of neighboring groups are much less common than in processes involving carbonium ions, and unequivocal examples appear to be restricted to the migration of an aryl group or a halogen atom.

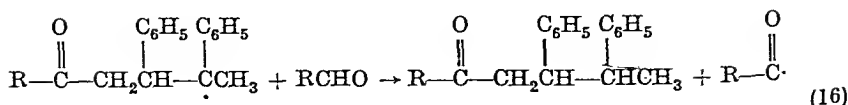
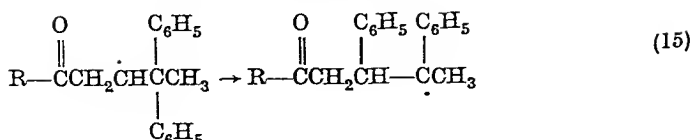
The only reported example of aryl migration in a radical addition is in the addition of *n*-butyraldehyde to 3,3-diphenyl-1-butene which gives propyl 2,3-diphenylbutyl ketone,¹⁵ presumably by the sequence shown. Similar rearrangements might be expected in comparable systems, but have not been investigated.



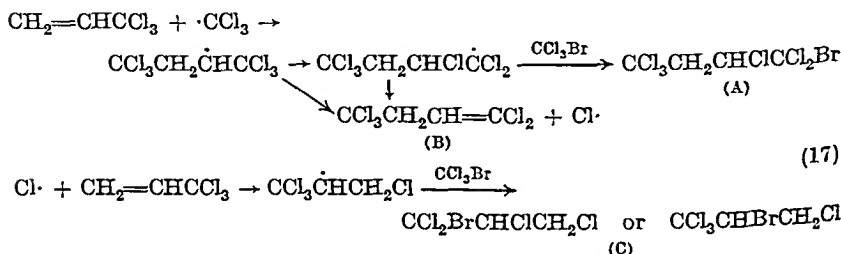
¹³ Kooymen and Farenhorst, *Rec Trav Chim*, **70**, 867 (1951)

¹⁴ Walling, "Free Radical Rearrangements," in P. DeMayo, *Molecular Rearrangements*, Interscience, New York, in press

¹⁵ Weinstock and Lewis, *J. Am. Chem. Soc.*, **79**, 6343 (1957)

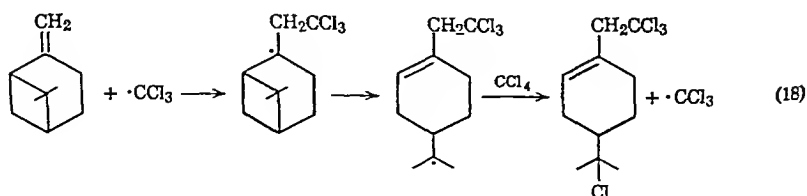


As an example of halogen migration, the addition of bromotrichloromethane to 3,3,3-trichloropropene gives a complex mixture of products (A, B, and C) which seems to require halogen migration as indicated.¹⁶



Since the structure of C was not unequivocally determined, occurrence of the second rearrangement remains in doubt.

Ring-opening reactions may take place in highly strained systems and are exemplified by the addition of carbon tetrachloride to α -pinene.¹⁷

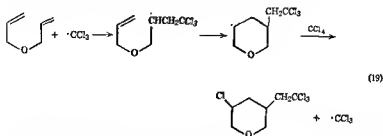


Similar products result from the addition of other carbon radicals, although with mercaptan additions where the displacement step is very rapid no ring opening occurs.

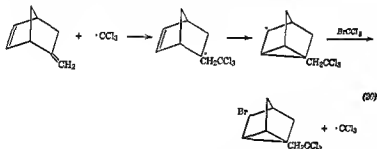
¹⁶ Nesmeyanov, Freidlina, and Zakharin, *Doklady Akad. Nauk USSR*, **81**, 199 (1951) [*C.A.*, **47**, 3789 (1953)].

¹⁷ Oldroyd, Fisher, and Goldblatt, *J. Am. Chem. Soc.*, **72**, 2407 (1950).

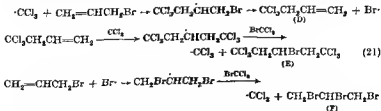
Ring closures, essentially the reverse of sequence (16), are also possible in additions to suitable dienes. Thus the reaction of carbon tetrachloride with diallyl ether follows the sequence shown.¹⁸



Similar processes have been reported. A tricycleno derivative is the predominant 1:1 addition product obtained in the reaction of bromotrichloromethane with 5-methylenebicyclo[2.2.1]hept-2-ene.¹⁹



Finally, additions are sometimes complicated by side reactions involving loss of halogen from intermediate radicals. Reaction sequence (17) provides an example, as does the addition of bromotrichloromethane to allyl bromide which yields D, E, and F.²⁰



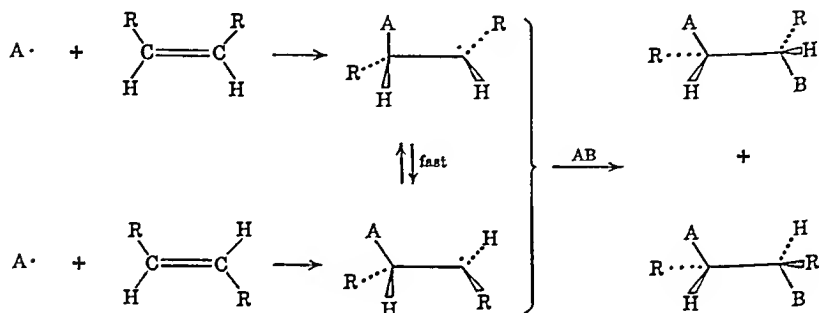
¹⁸ W. S. Friedlander, *Am. Chem. Soc. Meeting Abstr.*, **133**, 14N (1958).

¹⁹ Huyser and Echegaray, *J. Org. Chem.*, **27**, 429 (1962).

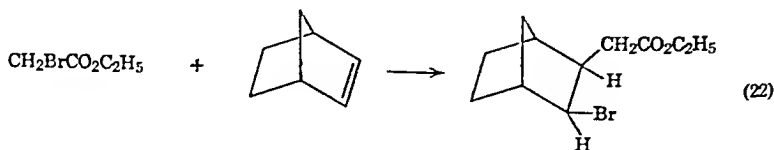
²⁰ Kharasch and Sage, *J. Org. Chem.*, **14**, 837 (1949).

Stereochemistry of Radical Additions

Radical additions to suitably substituted olefins can yield different possible stereoisomeric products: from open-chain olefins, *erythro* and *threo* pairs. In general, both pairs are obtained, and it is noteworthy that in all carbon-radical additions which have been investigated the same mixture is obtained starting from the *cis*- or the *trans*-olefin. The presumed explanation is that the intermediate radical undergoes free rotation about the former double bond at a rate which is rapid compared with reaction with the addend, AB.



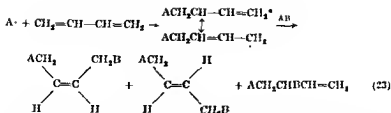
The stereochemistry of carbon radical additions to cyclic olefins has not been studied. However, the addition of hydrogen bromide and of mercaptans is preferably *trans*,* and a similar result might be expected with carbon radicals. Additions to the bridged norbornene system in contrast appear to give solely the *cis-exo* product, presumably for steric reasons, e.g., with ethyl bromoacetate.²¹



In additions to 1,3-dienes, attack of the resulting allylic radical on the addend can give rise to three possible products shown in (23). In general, 1,4 addition is preferred, but the relative amounts of *cis* and *trans* product have not been investigated in detail. From analogy to results in butadiene

* See Chapter 4, pp. 157 and 173.

²¹ J. Weinstock, *Am. Chem. Soc. Meeting Abstr.*, **123**, 19-O (1955).



polymerization²² and investigations of the stereochemistry of allylic radicals,²³ it might be expected that the *trans* product would predominate and its relative yield would be increased at lower temperatures.

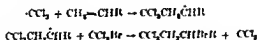
SCOPE AND LIMITATIONS

Polyhalomethanes (Tables V-VIII)

As a class, the polyhalomethanes have received the greatest amount of study in radical addition reactions. Most of the successful additions have involved a tri- or tetra-halomethane, and displacement occurs on halogen in the order $I > Br > Cl$. Thus with bromotrichloromethane the reaction follows the course



by way of the sequence



Reactions involving carbon tetrachloride and bromotrichloromethane are listed in Tables V and VI, respectively.

Iodo-trifluoromethane is the only trifluoromethane that gives good yields of addition product (Table VII).

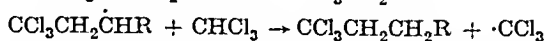
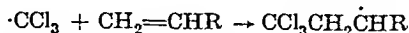


of higher molecular weight may be built up by a stepwise process (rather than telomerization).²⁴ While a four-center essentially non-radical reaction was suggested, it seems more likely that the products result from radical addition of initial 1:1 adducts to additional olefin.

Other polyhalomethane additions are listed in Table VIII. It is noteworthy that, in contrast to other polyhalomethanes, chloroform adds by hydrogen transfer; for example,



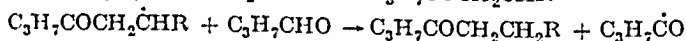
via



With polyhalomethanes less reactive than bromotrichloromethane, telomer formation is a serious complication in additions to simple olefins, although it can be minimized by working at high addend:olefin ratios. The other serious side reaction in halomethane additions is abstraction of allylic hydrogen, as discussed in the previous section.

Aldehydes (Table IX)

The addition of an aldehyde to an olefin results in the formation of a ketone.



In some cases, the yields of 1:1 adducts are fairly good. With simple olefins such as ethylene, telomer formation does occur. Polar effects are important, and higher yields may be expected from additions of a given aldehyde to an olefin that has electron acceptor properties. Perfluoro-olefins and olefins having carbonyl groups conjugated with the double bond fall in this category.

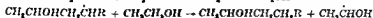
A side reaction which tends to lower the yields of ketones is the decarbonylation of the acyl radical.

Alcohols (Table X)

Primary and secondary alcohols add to olefins to form secondary and tertiary alcohols, respectively



via



Similarly,



The addition of methyl alcohol to olefins results in the formation of primary alcohols



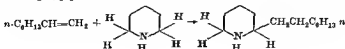
Tertiary alcohols, having no α -hydrogen atoms, do not add to olefins in a free radical chain reaction

In all reported additions of alcohols to alkenes telomers are formed. With perfluoroolefins, fairly high yields of 1:1 addition products can be obtained, presumably because of favorable polar contributions in the chain transfer reaction. The tendency toward telomer formation with a given olefin is $\text{CH}_3\text{OH} > \text{primary alcohol} > \text{secondary alcohol}$. With high alcohol to olefin ratios and a sufficiently high reaction temperature, fairly good yields of 1:1 adducts can be obtained with secondary alcohols.

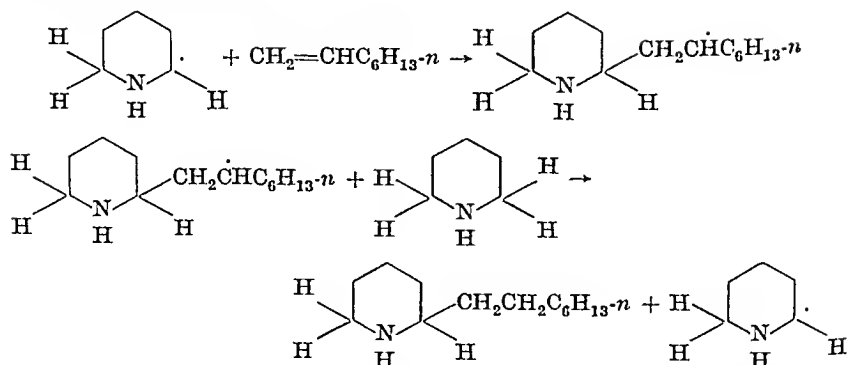
Although some photoinitiated additions of alcohols to olefins have been reported, the most notable success has been obtained with reactions initiated by di-*t*-butyl peroxide. Acyl peroxides undergo an induced decomposition with alcohols and are generally not effective initiators. (See the discussion of initiators, pp. 112-117) However, benzoyl peroxide has been used successfully to initiate additions of alcohols to perfluoroalkenes. Azobis(isobutyronitrile) is also ineffective as an initiator for alcohol additions, presumably because of the stability of the initiator radical

Amines (Table XI)

In contrast to most polar reactions of amines, their radical addition to olefins involves the hydrogen atom on a carbon atom bonded to nitrogen. For example, piperidine adds to 1-octene to form 2-octylpiperidine



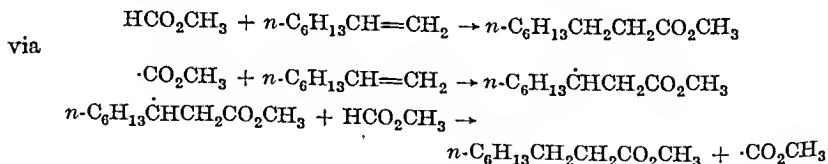
The chain sequence for this addition is



Additions of amines are generally initiated with di-*t*-butyl peroxide. Although some of these additions have been initiated photochemically, the reactions of amines with acyl peroxides render these peroxides ineffective as initiators. (See the discussion of initiators, pp. 112-117).

Formic Acid Derivatives (Table XII)

Methyl formate is the only formate ester which has led to isolable products in free radical addition reactions. In the addition of methyl formate to *n*-alkenes the carbonyl-bonded hydrogen atom, as in aldehydes, undergoes abstraction in the transfer step yielding methyl esters as addition products.



In all reported additions of methyl formate, a considerable amount of telomeric product was formed and yields of 1:1 addition product were somewhat modest at best.

Ethyl formate, although it participates in a chain reaction with ethylene, leads to a mixture of products. Not only the carbonyl-bonded hydrogen atom undergoes abstraction in the transfer step yielding ethyl esters as addition products, but the abstraction of a hydrogen atom from the alcohol portion of the ester also occurs yielding formic esters of telomeric secondary alcohols.

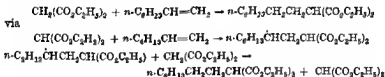
N-Alkyl formamides react to form a mixture of products. Abstraction of the carbonyl-bonded hydrogen atom in the transfer step results in the

formation of the N-alkyl amides of carboxylic acids. However, the transfer process can also involve the hydrogen atoms of the nitrogen-bonded alkyl portion of the molecule yielding telomeric N-alkyl formamides as products

The additions were initiated with di-*t*-butyl peroxide, benzoyl peroxide having proved ineffective. Attempts at photochemical initiation in the case of methyl formate were also unsuccessful, considerable amounts of carbon monoxide and methanol were formed.

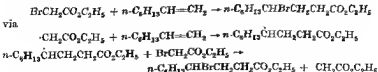
Esters and Acids (Table XIII)

A hydrogen atom of a methylene group such as that in malonic ester, acetoacetic ester, or methyl cyanoacetate is readily abstracted by free radicals. The resulting free radical readily adds to terminal olefins. A free radical chain sequence involving these reactions yields the alkylated ester. For example, malonic ester and 1-octene react to form *n*-octyl-malonic ester.



This method of alkylating active methylene compounds has been employed with success under proper experimental procedures (a high ratio of ester to olefin and a high reaction temperature), and 1:1 addition products have been obtained in good yield. Other esters and acids can also be alkylated in the α position in this manner.

Certain α -halo esters add to olefins in reactions involving the transfer of a halogen atom. For example, the addition of ethyl α -bromoacetate to 1-octene yields ethyl γ -bromocaproate.

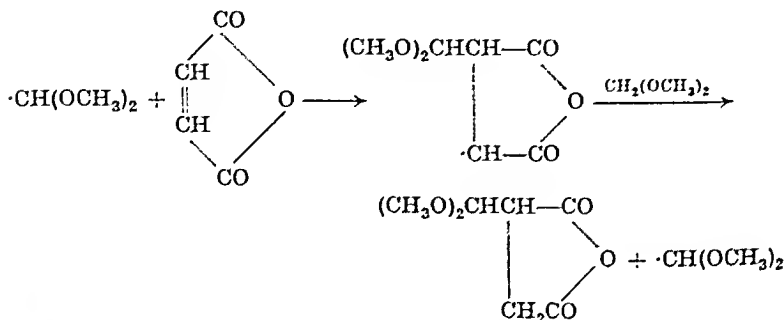


Other acid derivatives, e.g., nitriles and acid chlorides, undergo comparable reactions and are included in Table XV.

Most ester addition reactions have been initiated with di-*t*-butyl peroxide, although the reactions involving the halo esters were initiated with benzoyl peroxide and azobis(isobutyronitrile)

Ethers and Acetals (Table XIV)

The work in this area of Kharasch additions is somewhat limited and the examples are taken largely from the patent literature. These additions involve the hydrogen atoms on a carbon atom bonded to oxygen in the transfer step, and subsequent addition of the ether radical to the olefin in the chain sequence as shown for the addition of methylal to maleic anhydride.



Most successful additions of ethers or acetals are to unsaturated compounds that will give favorable polar contributions both in the addition and in the chain transfer steps of the chain sequence. Maleic anhydride, α,β -unsaturated esters, and perfluoroolefins have been used with success.

Miscellaneous Additions

A few other types of molecules which undergo radical addition to olefins are collected in Table XV. It is worth noting that, at very high temperatures and pressures, radical additions of simple alkanes to olefins occur, initiated either thermally or by high-energy radiation. However, since such reactions lie outside the range of usual laboratory practice, they are not treated in detail.

INITIATION

The factors involved in the initiation of Kharasch addition reactions are extremely important in determining yields and in dictating the choice of reaction conditions. The methods of initiation, i.e., the introduction of free radicals in the reaction mixture, can be divided into three general types: (1) chemical initiation, (2) photoinitiation, and (3) high-energy radiation. Chemical initiators have the advantages of ease of handling and modest equipment requirements but have disadvantages in their temperature requirements and in the side reactions they may undergo.

Photoinitiation and high-energy radiation are temperature-independent and do not require the addition of chemical reagents to the reaction mixture. However, they require more elaborate equipment

Chemical Initiators

Two chief types of initiators have been used to induce Kharasch addition reactions. organic peroxides and azobis(nitriles) The common feature of these materials is that, in the absence of any induced reactions, they can be

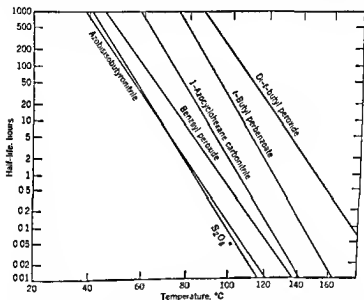


FIG. 3. Half-lives of some common initiators as a function of temperature. From C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957, p. 469

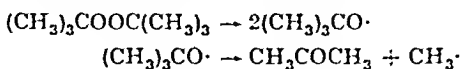
decomposed thermally into free radicals in a first-order reaction. Figure 3 shows the half-lives of some of the initiators useful in starting free radical chain reactions at ordinary temperatures (0–200°)

Since addition reactions require a continual supply of radicals to start chains, it is evident that with a given initiator a temperature should be chosen so that the desired reaction time corresponds to not more than a few half-lives of the initiator. Alternatively, the reaction may be carried out

at a higher temperature with continuous or incremental addition of the initiator.

The chemistry of these chemical initiators can best be discussed in terms of dialkyl peroxides, acyl peroxides, and azobis(nitriles).

Dialkyl Peroxides. The most readily available and widely used compound of this class is di-*t*-butyl peroxide (DTBP). This material undergoes the following smooth first-order decomposition both in solution and in the gas phase.

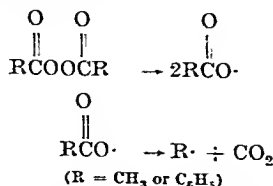


The extent of the secondary reaction is dependent on the reactivity of the solvent toward the *t*-butoxy radical formed in the primary reaction. The primary reaction, *which is rate-determining*, has a half-life of about 20 hours at 120°. The half-life decreases to about 1 hour at 150°, making this material a useful initiator in the temperature range 110–150°. This temperature range makes di-*t*-butyl peroxide useful in addition reactions involving an addend with a low chain transfer constant at lower temperatures. Indeed, the reason certain additions are feasible with di-*t*-butyl peroxide as the initiator may be that the temperature required to start the reaction is high enough to let the transfer reaction compete successfully with the polymerization step.

Advantages of di-*t*-butyl peroxide over acyl peroxides are that it shows little tendency to undergo induced decomposition and that its rate of decomposition is solvent independent. Furthermore, the radicals formed, *t*-butoxy radicals in the initial decomposition and methyl radicals in the possible elimination reaction, are both very reactive and capable of participating in steps which will start the desired free radical chain reaction.

Dicumyl peroxide, which is now commercially available, has received less study.

Acyl Peroxides. The most familiar examples of this class of peroxides are benzoyl peroxide and acetyl peroxide. These peroxides are thermally decomposed according to the scheme

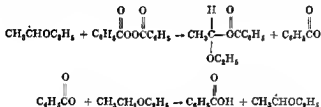


The decomposition of acetyl peroxide appears to proceed almost entirely to furnish methyl radicals and carbon dioxide. Benzoyl peroxide, on the

other hand, does give evidence of a benzoyloxy radical in its decomposition, and the amount of the secondary elimination reaction is dependent on the nature of the reagents with which the benzoyloxy radical may react.

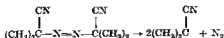
The first-order decomposition rate of these peroxides is such that they have reasonable half-lives in the range 50–100°. However, the rate of disappearance of an acyl peroxide is also dependent on its environment, certain solvents being capable of causing a rapid induced decomposition which renders most of the peroxide ineffective as an initiator for the desired chain reaction.

The chemistry of the induced decomposition of benzoyl peroxide by ethers was elucidated by Cass.²⁵ The ether radical formed by abstraction of an α -hydrogen atom by a peroxide radical fragment reacts very rapidly with unreacted peroxide, yielding 1-ethoxyethyl benzoate and propagating a chain reaction as shown in the reaction of benzoyl peroxide with diethyl ether.



Primary and secondary alcohols induce the decomposition of acyl peroxides in a similar manner with resulting oxidation of the alcohol to an aldehyde or ketone.²⁶ Acyl peroxides also react rapidly with amines, apparently chiefly by a non-radical path.²⁷ Because of these reactions acyl peroxides are obviously poor choices for the initiation of chain additions of ethers, alcohols, and amines to olefins. They have, however, been used successfully to initiate other additions; e.g., the lower-temperature requirements of acyl peroxides render them useful in additions of aldehydes where the higher temperature required by dialkyl peroxides might lead to excessive decarbonylation.

Azobis(nitriles). The most familiar example of this type of initiator is azobis(isobutyronitrile). This compound undergoes a first-order decomposition in the manner shown. The decomposition rate is not affected by



²⁵ Cass, *J. Am. Chem. Soc.*, **69**, 500 (1947).

²⁶ Kharsach, Friedlander, and Urry, *J. Org. Chem.*, **14**, 91 (1949).

²⁷ Walling and Indictor, *J. Am. Chem. Soc.*, **80**, 5814 (1958).

the environment, the material decomposing at essentially the same rate in a variety of solvents. The half-life of azobis(isobutyronitrile) is about 20 hours at 60° making it useful as an initiator in the temperature range from 40° to 80°. By varying the substituents, azobis(nitriles) that decompose at other temperatures may be obtained.

Although azobis(isobutyronitrile) does not show induced decomposition the resulting *cyanoisopropyl* radical is quite unreactive, so its efficiency as an initiator is often quite low. Accordingly its use is restricted to highly reactive olefins or addends such as bromotrichloromethane.

Other Chemical Initiators. A variety of other compounds are known which undergo thermal decomposition into radicals and might be expected to induce radical addition processes, but they have not been investigated in detail. Peresters such as *t*-butyl perbenzoate decompose at rates intermediate between dialkyl and diacyl peroxides. Hydroperoxides also yield radicals, but at rates which appear to be highly solvent-dependent and which are also complicated by induced decomposition. A number of radical-producing redox systems are known, such as the combination of ferrous ion and hydroperoxide, which reacts as follows.



All of these can undoubtedly be used in suitable systems and it is worth noting that some olefin-addend systems often react spontaneously on heating, perhaps as the result of dissociation of adventitious peroxidic impurities.

Photoinitiation

Ultraviolet light has been used successfully in many instances to initiate free radical addition reactions. On absorbing electromagnetic radiation a compound is excited to a higher electronic energy level. The amount of energy absorbed depends on the frequency of the radiation according to the relation

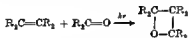
$$E = h\nu$$

where h is Planck's constant and ν is the frequency of the vibration. In the ultraviolet range (4000–2000 Å), the energy absorbed amounts to 71.4–142.8 kcal/mole. This is sufficient to rupture covalent bonds in an organic compound. Most organic compounds absorb radiation in this range, but the absorption does not necessitate a dissociation into free radicals. Other non-radical reactions or phenomena associated with absorption such as fluorescence or loss of the absorbed energy in collision with other molecules, particularly in the liquid phase, can also serve as

outlets for the absorbed energy. In some cases, however, the molecule is dissociated directly on absorption of light into free radicals, and light serves as a useful means of initiation.

The feasibility of using light to initiate the free radical reaction is dependent on the system involved. Some compounds absorb light in the near ultraviolet (3000 Å or above) and are dissociated very readily into free radicals. Bromotrichloromethane is one good example, and additions of this compound are readily initiated by illuminating reaction mixtures with ordinary sunlight or with a commercial sunlamp. Pyrex, however, is not transparent to light of shorter wavelength than 3000 Å. If the reactants require light below the lower limit of transparency of Pyrex, another container such as quartz, which is transparent to ultraviolet irradiation, is required. Production of ultraviolet light of lower wavelengths requires mercury vapor lamps or some other source of illumination.

Photoinitiation has proved useful in several addition reactions of polyhalomethanes and certain alcohols and amines. The ultraviolet absorption characteristics of other compounds suggest the feasibility of photoinitiated addition reactions. However, the possibility of photochemical reactions other than the desired initiation process exists. For example, methyl formate when illuminated undergoes extensive decomposition into carbon monoxide and methyl alcohol with no detectable amount of addition product in the presence of 1-octene. Aldehydes and ketones illuminated in the presence of non-terminal olefins and acetylenes yield derivatives of trimethylene oxide.²³



High-Energy Radiation

The use of α and β particles, γ rays, and x-rays to initiate free radical chain reactions has received a considerable amount of attention in the last few years. The effect of such high-energy radiation on organic matter is complex and involves initially chiefly the stripping of electrons from molecules to form ions. However, in secondary processes a significant amount of the total energy absorbed (up to perhaps 20%) may go into the homolytic cleavage of bonds to form radicals. These radicals in turn can induce radical addition processes, but the often low radical yields and the complex equipment and shielding required make the technique rather marginal for synthetic purposes except under rather special conditions.

²³ Buchi, Isman, and Lipensky, *J. Am. Chem. Soc.*, **78**, 4327 (1954).

EXPERIMENTAL CONDITIONS

Purity of Reagents

Since the reactions with which we are dealing are chain processes, traces of impurities which can interrupt chains can greatly lower yields or prolong reaction times. Accordingly, it is generally desirable to work with freshly distilled reagents of known purity. Reactive monomers such as vinyl acetate and styrene must be freed of inhibitors that have been added to prevent polymerization during storage. Phenolic inhibitors can be removed by extraction with dilute aqueous base before distillation. In some cases, trace impurities which cannot be readily removed can effectively be "burned up" by the use of additional initiator. Since oxygen commonly interferes with radical chain processes, yields may be improved and reactions accelerated by the use of an inert atmosphere or by vigorous boiling to displace air from the system. Metal salts may also interfere in some systems, and when reactions fail in metal vessels contamination should be suspected.

Concentration of Reactants

The most serious side reaction encountered in attempting to prepare simple 1:1 addition products is the formation of telomers. Telomers result from addition of the adduct radical to another molecule of olefin instead of chain transfer with a molecule of adding reagent. The rate of the addition reaction can obviously be minimized by lowering the concentration of the olefin. Consequently, in systems where the chain transfer constant is less than one, it is preferable to use a high molar ratio of adding reagent to olefin. One method of accomplishing this is to add the olefin to the reaction mixture very slowly, allowing the previously added portion to undergo almost complete reaction before more olefin is added. This procedure has made possible the formation of 1:1 addition products in good yields even with highly polymerizable monomers such as vinyl acetate. Where experimental conditions prohibit such slow addition, it is advisable to begin with a high concentration of the adding reagent with respect to the olefin.

Temperature

When telomer formation is a serious complication, it can often be diminished by increasing the reaction temperature. Thus many addition reactions which give low yields of 1:1 addition products at 50–80°, a temperature range suitable for such initiators as benzoyl peroxide, acetyl

peroxide, and azobis(isobutyronitrile), might be expected to give higher yields if initiated with di-*t*-butyl peroxide, an initiator effective in the range 120–150°

Complications may, of course, arise in carrying out reactions with low-boiling reagents at elevated temperatures. In some cases, slow addition of the more volatile component is satisfactory, as in the reaction of vinyl acetate with dimethyl malonate. Otherwise, the use of pressure equipment is required.

EXPERIMENTAL PROCEDURES

t-Amyl Alcohol (Addition of Isopropyl Alcohol to Ethylene).²⁹

A solution of 4.5 g. (0.03 mole) of di-*t*-butyl peroxide in 425 g. (7.07 moles) of isopropyl alcohol is heated to 125–130° in a glass-lined stainless steel autoclave. A pressure of ethylene of 200–300 lb./sq. in. is maintained above the solution and the gas is mixed with the liquid by means of a Magnedash stirrer. In 20 hours, approximately 2.0 moles of ethylene reacts. Distillation of the reaction mixture yields a low-boiling fraction consisting of the peroxide decomposition products, acetone and *t*-butyl alcohol. After removal of the unreacted isopropyl alcohol by distillation, the 1:1 addition product is collected at 66°/165 mm. The yield of *t*-amyl alcohol (n_D^{20} 1.4052) is 76 g., 36% based on the ethylene reacted.

Further fractionation of the reaction mixture gives 24.2 g. of the 2:1 addition product, 2-methyl-2-hexanol (82°/80 mm., n_D^{20} 1.4180); 16.0 g. of the 3:1 addition product, 2-methyl-2-octanol (66°/8 mm., n_D^{20} 1.4282); and 10.5 g. of the 4:1 addition product, 2-methyl-2-decanol (75°/0.3 mm., n_D^{20} 1.4368). A residue of 18.5 g. with an average molecular weight of 274 remains.

3,3-Dicarbomethoxypropyl Acetate (Addition of Dimethyl Malonate to Vinyl Acetate).³⁰ In a 500-ml. flask equipped with a condenser and a dropping funnel, 198 g. (1.5 moles) of dimethyl malonate is heated to 150–152°. A mixture of 12.9 g. (0.15 mole) of vinyl acetate and 4.4 g. (0.03 mole) of di-*t*-butyl peroxide is added from the dropping funnel to the heated ester during 4 hours. The reaction mixture is heated for an additional 30 minutes, then the peroxide decomposition products and unreacted dimethyl malonate are removed by vacuum distillation. Fractionation of the high-boiling residue yields 21 g. (65% based on vinyl acetate) of 3,3-dicarbomethoxypropyl acetate (108–115°/3 mm., n_D^{20} 1.4370, mol. wt. 216). About 0.5 g. of tetramethyl ethane-1,1,2,2-tetracarboxylate (m.p. 135°) and 19.0 g. of a telomeric residue having an average molecular weight of 468 are also obtained.

²⁹ Urry, Stacey, Kuyser, and Jureland, *J. Am. Chem. Soc.*, **78**, 450 (1956).

³⁰ R. Gritter, Ph. D. Thesis, University of Chicago, 1955.

1-Iodoheptafluoropropane (Addition of Trifluoroiodomethane to Perfluoroethylene).³¹ A mixture of trifluoroiodomethane and perfluoroethylene in a 10:1 molar ratio is sealed in a Pyrex reaction tube. The liquid phase of the mixture is exposed to ultraviolet radiation for 3 hours, after which the reaction mixture is recharged with the same quantity of olefin and the illumination repeated for 3 hours. After removal of the unreacted trifluoroiodomethane, the 1:1 addition product, 1-iodoheptafluoropropane, is collected at 39–40°. The yield is 94%, based on the olefin added.

Diethyl *n*-Butyrylsuccinate (Addition of *n*-Butyraldehyde to Diethyl Maleate).³² A mixture of 72.0 g. (1.0 mole) of *n*-butyraldehyde, 43.0 g. (0.25 mole) of diethyl maleate, and 2.0 g. (0.008 mole) of benzoyl peroxide is heated at the reflux temperature for 18 hours. During the heating, the temperature rises from 82° to 88°. The reaction mixture is cooled, extracted with aqueous sodium bicarbonate, washed twice with water, and dried over sodium sulfate. Removal of the unreacted aldehyde by distillation gives the crude 1:1 addition product, diethyl *n*-butyrylsuccinate (47 g., 76%, b.p. 95–108°/0.5 mm.), and 12 g. of a higher-boiling, yellow, slightly viscous residue. Redistillation of the crude diethyl *n*-butyrylsuccinate gives 32 g. of pure product; b.p. 112–114°/1 mm., n_D^{25} 1.4349.

1,1,1-Trichloro-3-bromo-3-phenylpropanol (Addition of Bromotrichloromethane to Styrene).³³ A solution of 100 g. of bromotrichloromethane, 12 g. of styrene, and 2.3 g. of acetyl peroxide is heated to 60–70° for 4 hours. Distillation of the reaction mixture through a 10-in. Vigreux column gives 78 g. of unreacted bromotrichloromethane (b.p. 103–104°) and 27 g. of 1,1,1-trichloro-3-bromo-3-phenylpropane (b.p. 92°/0.2 mm.). The adduct quickly solidifies to a white crystalline mass and, after one recrystallization from methanol, melts at 54.5–55.0°. After removal of the 1:1 addition product, 6 g. of a high-boiling residue remains.

1,1,1,3-Tetrachlorononane (Addition of Carbon Tetrachloride to 1-Octene).³⁴ Carbon tetrachloride (154 g., 1.0 mole), 1-octene (37 g., 0.33 mole), and benzoyl peroxide (5 g., 0.02 mole) are heated under reflux for 4 hours under a positive pressure of nitrogen (15 cm. of mercury). During the heating, the temperature rises from 90° to 105°. Removal of excess carbon tetrachloride by distillation leaves a residue which yields on vacuum distillation 72 g. of crude 1:1 addition product

³¹ Haszeldine, *J. Chem. Soc.*, 1953, 3761.

³² Patrick, *J. Org. Chem.*, 17, 1009 (1952).

³³ Kharasch, Reinmuth, and Urry, *J. Am. Chem. Soc.*, 69, 1105 (1947).

³⁴ Kharasch, Jensen, and Urry, *J. Am. Chem. Soc.*, 69, 1100 (1947).

(b p 75–85°/0.05 mm) and 13 g of higher telomers. Redistillation of the crude product gives 66 g (75%) of 1,1,1,3-tetrachlorononane, b p 78–79°/0.1 mm, n_D^{20} 1.4770.

TABULAR SURVEY

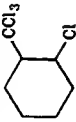
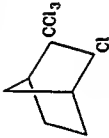
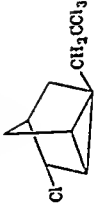
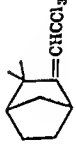
The following tables list various addition reactions according to the type of addend. They include reactions that could be found in a literature survey up to April 1962. *Chemical Abstracts* were covered in this survey up to January 1962. The reactions chosen for this tabulation are those which yielded simple addition products with the indicated unsaturated species. In some cases a reaction which led to telomeric products was included to illustrate that addition does occur to the unsaturated compound listed.




In tables containing several addends, the addends are listed in order of increasing number of carbon atoms. The unsaturated compounds are listed in the following order: alkenes and alkynes in order of increasing number of carbon atoms, halogenated alkenes, unsaturated compounds with oxygen-containing functions, and, finally, unsaturated compounds with other atoms. The method of initiation of the reactions is indicated, where possible, by the following symbols: Bz_2O_2 , benzoyl peroxide; Ac_2O_2 , acetyl peroxide; DTBP, di-*t*-butyl peroxide; AIBN, azobis(isobutyronitrile); $h\nu$, photoinitiation; Thermal, thermal initiation; γ , initiation by gamma rays; and Per., peroxidic agents, generally benzoyl or acetyl peroxide.

The yield of addition product listed is the highest reported under the experimental conditions in the indicated reference. The experimental conditions are not listed in these tables (however, see the following paragraph), since it is the authors' belief that in many cases they are not the optimum conditions. Proper modifications of the experimental procedure, such as varying the ratio of addend to unsaturated compound or raising the temperature, might in many cases result in considerable increase in the yield of the 1:1 addition product. The yields reported in the tables do, however, indicate to some degree the potential synthetic usefulness of the reaction.

Some information about reaction temperatures can be obtained from the initiator used. Reactions initiated with benzoyl peroxide were generally carried out at 60–90°. The same temperature range is generally employed for reactions initiated by acetyl peroxide and azobis(isobutyronitrile), although in some instances slightly lower temperature (<50°) are possible. Reactions induced with di-*t*-butyl peroxide were carried out at 110–160°, a temperature range in which the peroxide yields free radicals at a rate useful for starting chains.





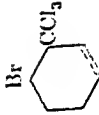
TABLE V
ADDITION OF CARBON TETRACHLORIDE




Olefin	Initiator	1:1 Addition Product(s)	Yield of 1:1 Adduct, % (Tolomers)	Refs.
Ethylene	Bz_2O_2	$Cl_3CCH_2CH_2Cl$	80	34-37
Propylene	Bz_2O_2	$Cl_3CCH_2CHClCH_3$	plus tolomers	38
Isobutylene	Bz_2O_2	$Cl_3CCH_2CCl(CH_3)_2$	78	39, 40
1,3-Butadiene	Bz_2O_2	$Cl_3CCH_2CH=CHCH_2Cl$	23	41
<i>n</i> -Butylethylene	Bz_2O_2	$Cl_3CCH_2CHClC(CH_3)_3$	—	42
Biallyl	—	$Cl_3CCH_2CHCl(CH_2)_2CH=CH_2$ $Cl_3CCH_2CHCl(CH_2)_2CHClCH_2CCl_3$	26	34
			31	
Cyclohexene	Bz_2O_2		—	42, 43
1-Heptene	Bz_2O_2	$Cl_3CCH_2CHClC_5H_{11-n}$	72	42, 44
Norbornene	Bz_2O_2		56	45
1-Octene	Ac_2O_2	$Cl_3CCH_2CHClC_6H_{13-n}$	85	34, 46
5-Methylenecyclo[2.2.1]hept-2-ene	Bz_2O_2		—	19
Camphene	Ac_2O_2		—	47, 48

Limonene		Br_2O_2	70	49, 50
β -Pinene		Br_2O_2	97	50-52
Allylbenzene	Ac_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OC}_2\text{H}_5$	25	53
o-Methoxyallylbenzene	Ac_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{C}_6\text{H}_4\text{OCH}_3$	50	53
p-Methoxyallylbenzene	Ac_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{C}_6\text{H}_4\text{OCH}_3$	23	53
m-Methoxyallylbenzene	Ac_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{C}_6\text{H}_4\text{OCH}_3$	24	53
p-Methoxyallylbenzene	Ac_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{C}_6\text{H}_4\text{OCH}_3$	29	53
1-Hexadecene	Br_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{C}_6\text{H}_4\text{OCH}_3$	—	42
Allyl chloride	Br_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{Cl}$	(Telomers)	39
Vinyl acetate	Br_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OCCH}_3$	(Telomers)	54, 55
Allyl acetate	Br_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OCCH}_3$	(Telomers)	33, 39
Vinyl ethyl ether	Br_2O_2	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OC}_2\text{H}_5$	53	56
Vinyl n-butyl ether	$\text{AlBN}, h\nu$	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OC}_4\text{H}_9$	95	56, 57
Vinyl cyclohexyl ether	$\text{AlBN}, h\nu$	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OC}_6\text{H}_{11}$	90	57
Vinyl phenyl ether	$\text{AlBN}, h\nu$	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OC}_6\text{H}_5$	87	56, 57
Divinyl ether	AlBN	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{O}$	50	58
$\text{CH}_2=\text{CHCH}(\text{OC}_2\text{H}_5)_2$	$h\nu$	$\text{Cl}_2\text{CH}_2\text{CHClCH}_2\text{OC}_2\text{H}_5$	—	59
$\text{ClCH}=\text{CHCH}_2\text{Cl}$	$\text{Ac}_2\text{O}_2, \text{Br}_2\text{O}_2$	$\text{Cl}_2\text{CH}=\text{CHCl}$	46	60
$(\text{CCH}=\text{CH})_2\text{Hg}$	$\text{Ac}_2\text{O}_2, \text{Br}_2\text{O}_2$	$\text{Cl}_2\text{CH}=\text{CHCl}$	36	60
$\text{CH}_2=\text{CHB}(\text{OC}_2\text{H}_5)_2$	AlBN	$\text{Cl}_2\text{CH}_2\text{CHClB}(\text{OC}_2\text{H}_5)_2$	45	61
Butadiene sulfone	Br_2O_2	 + $\text{Cl}_2\text{CH}_2\text{CH}=\text{CHCH}_2\text{Cl}$	62	41, 62

Note. References 35 to 160 are on pp. 147-149.


TABLE VI
ADDITION OF BROMOTRICHLOROMETHANE


Unsaturated Compound	Initiation	Product(s)	Yield, %	Refs.
Ethylene	Ac_2O_2	$\text{Cl}_3\text{CCH}_2\text{CH}_2\text{Br}$	—	33, 63
Propylene	<i>hr</i>	$\text{Cl}_3\text{CCH}_2\text{CHBrCH}_3$	—	33
1-Butene	—	$\text{Cl}_3\text{CCH}_2\text{CHBrC}_2\text{H}_5$	43	63
2-Butene	<i>hr</i>	$\text{CH}_3\text{CH}(\text{CCl}_3)\text{CHBrCH}_3$	13	64
Isobutylene	Ac_2O_2	$\text{Cl}_3\text{CCH}_2\text{CBr}(\text{CH}_3)_2$	—	33
1,3-Butadiene	—	$\text{Cl}_3\text{CCH}_2\text{CH}=\text{CHCH}_2\text{Br}$	75	65, 66
2-Methyl-2-butene	<i>hr</i>	$\text{Cl}_3\text{CCH}(\text{CH}_3)\text{CBr}(\text{CH}_3)_2$	77	65
Cyclopentene	—		—	67
Cyclopentadiene	—		—	67
2-Ethyl-1-butene	—	$\text{Cl}_3\text{CCH}_2\text{CBr}(\text{C}_2\text{H}_5)_2$	91	65
Cyclohexene	<i>hr</i>		30	65, 67, 68
1,3-Cyclohexadiene	—		68	67
			32	

Norbornene	—		—	67
1-Octene	$h\nu$, Ac_2O_2	$Cl_3CCH_2CHBrC_4H_9$	88	33, 65
2-Octene	Ac_2O_2	$C_8H_{16}Cl_2Br$	45	69
1-Octyne	Ac_2O_2	$Cl_3CCH=CBrc-C_4H_9$	80	69
2-Octyne	Ac_2O_2	$C_8H_{16}Cl_3Br$	33	69
Bicyclo[2.2.2]oct 2-ene	—		—	67
Styrene	Ac_2O_2	$Cl_3CCH_2CHBrC_6H_5$	78	33, 65, 66
Phenylacetylene	—	$Cl_3CH=CBrc-C_6H_5$	32	70
α -Methylstyrene	$h\nu$	$Cl_3CCH=C(CH_3)C_6H_5$	40	66
β -Methylstyrene	$h\nu$	$Cl_3CCH(CH_3)CHBrC_6H_5$	—	65
Allylbenzene	$h\nu$	$Cl_3CCH_2CHBrCH_2C_6H_5$	44	65
Indene	—		—	67
Dicyclopentadiene	—	$C_{10}H_{12}Cl_3Br$	—	67
$CF_2=CFCl$	—	$Cl_2CCF_2CFCHBr$	—	71
$CF_2=CHCH_3$	$h\nu$	$Cl_3CCH(CH_3)CF_2Br$	—	72
$CH_2=CHCF_3$	—	$Cl_3CCH_2CHBrCF_3$	—	73
Allyl chloride	—	$Cl_3CCH_2CHBrCH_2Cl$	—	33, 65
$CH_2=CClCH_3$	Ac_2O_2	$Cl_3CCH_2CClBrCH_3$	—	74
$CH_2=CClCH_2Cl$	Bz_2O_2	$Cl_3CCH_2CClBrCH_2Cl$	34	74
$CHCl=CHCCl_3$	Bz_2O_2	$Cl_3CCHClCHBrCCl_3$	8	74
			65	74

Note References 35 to 160 are on pp. 147-149.

TABLE VI—Continued
ADDITION OF BROMOTRICHLOROMETHANE

Unsaturated Compound	Initiation	Product(s)	Yield, %	Refs.
Allyl bromide	$h\nu$	$\text{Cl}_3\text{CCH}_2\text{CHBrCH}_2\text{CCl}_3$ $\text{Cl}_3\text{CCH}_2\text{CH}=\text{CH}_2$ $\text{BrCH}_2\text{CHBrCH}_2\text{Br}$	37 — 41	70
$\text{CH}_2=\text{CBrCH}_3$	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CBr}_2\text{CH}_3$	50	74
$\text{CH}_2=\text{CBrCH}_2\text{Cl}$	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CBr}_2\text{CH}_2\text{Cl}$	8	74
$\text{CH}_2=\text{C}(\text{CF}_3)\text{CH}_3$	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CBr}(\text{CF}_3)\text{CH}_3$	64	74
$\text{CH}_2\text{CH}=\text{CClCH}_2$	Bz_2O_2	$\text{Cl}_3\text{CCH}(\text{CH}_3)\text{CClBrCH}_3$	76	74
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$	$h\nu$	$\text{Cl}_3\text{CCH}_2\text{CBr}(\text{CH}_3)\text{CH}_2\text{Cl}$	45	74
$\text{CH}_3\text{CHCH}=\text{CHCH}_2\text{Cl}$	Bz_2O_2	$\text{CH}_2\text{CH}(\text{CH}_3)\text{CHBrCH}_2\text{Cl}$	23	74
$\text{CH}_3\text{CHCH}=\text{CClCH}_3$	Bz_2O_2	$\text{CH}_2\text{CH}(\text{CCl}_3)\text{CCHBrCH}_3$	8	74
$\text{CH}_2=\text{CHCH}_2\text{CCl}_3$	$h\nu$	$\text{Cl}_3\text{CCH}_2\text{CHBrCH}_2\text{CCl}_3$	—	65
<i>p</i> -Chlorostyrene	$h\nu$	$\text{Cl}_3\text{CCH}_2\text{CHBrC}_6\text{H}_4\text{Cl-}p$	74	66
2,4-Dichlorostyrene	$h\nu$	$\text{Cl}_3\text{CCH}_2\text{CHBrC}_6\text{H}_3\text{Cl}_2-2,4$	20	65
Allyl ethyl ether	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CHBrCH}_2\text{OC}_2\text{H}_5$	29	75
Diallyl ether	—		—	76
Allyl β -chloro- α,β -trifluoroethyl ether	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CHBrCH}_2\text{OCF}_2\text{CH}_2\text{Cl}$	50	75
Vinyl acetate	Ac_2O_2 or $h\nu$	$\text{Cl}_3\text{CCH}_2\text{CHBrCOOCH}_3$	90	33, 63, 65, 77, 78

Isopropenyl acetate $\text{CH}_2=\text{CH}_2\text{OCOCH}_3$	Bz_2O_2 or $h\nu$ AIBN	$\text{Cl}_3\text{CCH}_2\text{CB}(\text{CH}_3)\text{OCOCH}_3$	27	66
$\text{CH}_2=\text{CHCH}_2\text{CO}_2\text{C}_2\text{H}_5$	$h\nu$	$\text{Cl}_3\text{CCH}=\text{CB}(\text{CH}_3)\text{OCOCH}_3$	—	79
$\text{CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CHB}(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5$	92	65
Dimethyl fumarate	$h\nu$	$\text{CH}_3\text{CH}(\text{CO}_2\text{CH}_3)\text{CHB}(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5$	84	80
		$\text{Cl}_3\text{CCHCO}_2\text{CH}_3$	—	81, 82
Dimethyl maleate	$h\nu$	$\text{BrCHCO}_2\text{CH}_3$ $\text{Cl}_3\text{CCHCO}_2\text{CH}_3$	—	81
Ethyl cinnamate	Ac_2O_2 or Bz_2O_2 $h\nu$	$\text{BrCHCO}_2\text{CH}_3$ $\text{Cl}_3\text{CCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CHB}(\text{CH}_3)\text{H}$	72	65, 80
Allyl cyanide	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CHB}(\text{CH}_3)\text{CN}$	95	65
cis-Cinnamionitrile	Bz_2O_2	$\text{Cl}_3\text{CCH}(\text{CN})\text{CHB}(\text{CH}_3)\text{H}$	—	80
trans-Cinnamionitrile	Bz_2O_2	$\text{Cl}_3\text{CCH}(\text{CN})\text{CHB}(\text{CH}_3)\text{H}$	33	80
Butadiene sulfone	Ac_2O_2	Br  SO_3	62	62
$\text{CH}_2=\text{CHSiCl}_3$	Bz_2O_2 $h\nu$	$\text{Cl}_3\text{CCH}_2\text{CHB}(\text{CH}_3)\text{SiCl}_3$	—	83
$\text{CH}_2=\text{CHSi}(\text{Cl}_2)\text{CH}_3$	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CHB}(\text{CH}_3)\text{Si}(\text{Cl}_2)\text{CH}_3$	—	83
$\text{CH}_2=\text{CHSi}(\text{C}_6\text{H}_5)_2$	AIBN	$\text{Cl}_3\text{CCH}_2\text{CHB}(\text{CH}_3)\text{Si}(\text{C}_6\text{H}_5)_2$	94	84
$\text{CH}_2=\text{CHB}(\text{OC}_4\text{H}_9)_2$	AIBN	$\text{Cl}_3\text{CCH}_2\text{CHB}(\text{CH}_3)\text{B}(\text{OC}_4\text{H}_9)_2$	94	61
$\text{CH}_2=\text{C}(\text{CH}_3)\text{B}(\text{OC}_4\text{H}_9)_2$	AIBN	$\text{Cl}_3\text{CCH}_2\text{CB}(\text{CH}_3)\text{B}(\text{OC}_4\text{H}_9)_2$	90	85
$\text{CH}_3\text{CH}=\text{CHB}(\text{OC}_4\text{H}_9)_2$	AIBN	$\text{Cl}_3\text{CCH}(\text{CH}_3)\text{CHB}(\text{CH}_3)\text{B}(\text{OC}_4\text{H}_9)_2$	—	85
$\text{CH}_2=\text{CHSn}(\text{C}_6\text{H}_5)_3$	Bz_2O_2	$\text{Cl}_3\text{CCH}_2\text{CHB}(\text{CH}_3)\text{Sn}(\text{C}_6\text{H}_5)_3$	94	84

Note. References 35 to 100 are on pp. 147-149.

TABLE VII
 ADDITION OF IODOTRIFLUOROMETHANE

Unsaturated Compound	Initiator	Product(s)	Yield, %	Refs.
$\text{CH}_2=\text{CH}_2$	<i>h\nu</i> or thermal	$\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$	82	86
$\text{CH}\equiv\text{CH}$	<i>h\nu</i>	$\text{CF}_3\text{CH}=\text{CHI}$	78	87, 88
$\text{CH}_2=\text{CH}\text{I}$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{CHI}$	65	89
$\text{CH}_2=\text{CHCl}$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{CHClI}$	47	89
$\text{CH}_2=\text{CF}_2$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{CF}_2\text{I}$	80	24
$\text{CF}_2=\text{CHCl}$	<i>h\nu</i>	$\text{CF}_3\text{CF}_2\text{CHClI}$	—	90
$\text{CH}_2=\text{CF}_2$	—	$\text{CF}_3\text{CHFCF}_2\text{I}$	80	91
		$\text{CF}_3\text{CF}_2\text{CHFI}$	20	
	<i>h\nu</i>	$\text{CF}_3\text{CF}_2\text{CFCH}$	Telomers	92, 93
	<i>h\nu</i>	$\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$		86, 94, 95
$\text{CH}_2=\text{CHCHCH}_3$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{CHCHCH}_3$	94	86
$\text{CH}_2=\text{CHCHCF}_3$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{CHCHCF}_3$	50	
$\text{CF}_2=\text{CHCHCH}_3$	<i>h\nu</i> or thermal	$\text{CF}_3\text{CH}(\text{CH}_3)\text{CHCF}_3$	68	72, 96
$\text{CF}_2=\text{CHCF}_3$	<i>h\nu</i>	$\text{CF}_3\text{CH}(\text{CH}_3)\text{CF}_3\text{I}$	77	97
$\text{CF}_2=\text{CHCF}_3$	<i>h\nu</i>	$(\text{CF}_3)_2\text{CHCF}_3\text{I}$	80	98
$\text{CF}_2=\text{CHCF}_3$	<i>h\nu</i>	$\text{CF}_3\text{CF}_2\text{CHCF}_3$	Telomers	99, 100
$\text{CH}\equiv\text{CCl}_3$	<i>h\nu</i>	$\text{CF}_3\text{CH}=\text{CClCH}_3$		101, 102
$\text{CH}\equiv\text{CCF}_3$	<i>h\nu</i>	$\text{CF}_3\text{CH}=\text{CCF}_3$	—	102
$\text{CH}_2=\text{C}(\text{CF}_3)_2$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{C}(\text{CF}_3)_2$	71	97
$\text{CH}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{Cl}$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{C}(\text{CF}_3)\text{CF}_2\text{Cl}$	69	97
$\text{CH}\equiv\text{CC}_2\text{H}_5$	<i>h\nu</i>	$\text{CF}_3\text{CH}=\text{CC}_2\text{H}_5$	—	102
$\text{CH}_2=\text{CHCN}$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{CHCN}$	72	103
$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	<i>h\nu</i>	$\text{CF}_3\text{CH}_2\text{CHCO}_2\text{CH}_3$	38	89

Note: References 35 to 160 are on pp. 147-149.

TABLE VIII
ADDITION OF OTHER POLYHALOALKANES

Polyhaloalkane	Unsaturated Compound	Initiator	Product(s)	Yield, %	Refs
CH_2ClI	$\text{CH}_2=\text{CH}_2$	—	$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{I}$	Telomers	35
CHCl_3	$\text{CH}_2=\text{CH}_2$	—	$\text{OCCl}_2\text{CH}_2\text{CH}_3$	Telomers	35, 37
	$\text{CH}_2=\text{CHCH}_3$	Bz_2O_2	$\text{OCCl}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$	Telomers	6
	1,3 Butadiene	Ac_2O_2	$\text{OCCl}_2\text{CH}_2\text{CH}=\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$	45	104
	$(\text{CH}_2=\text{CHCH}_2)_2$	Ac_2O_2	$\text{C}_4\text{H}_8\text{OCl}_2$	45	
	$\text{CH}_2=\text{CHC}_6\text{H}_{13}{}^n$	Bz_2O_2	$\text{OCCl}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_{13}{}^n$	5	34
CHCl_2Br	$\text{CH}_2=\text{CHCH}_3$	—	$\text{CHCl}_2\text{CH}_2\text{CHBrCH}_3$	22	34
	$\text{CH}_2=\text{C}(\text{CH}_3)_2$	—	$\text{CHCl}_2\text{CH}_2\text{CBr}(\text{CH}_3)_2$	—	105
	$\text{CH}_2=\text{CHC}_6\text{H}_{13}{}^n$	—	$\text{CHCl}_2\text{CH}_2\text{CHBrC}_6\text{H}_{13}{}^n$	—	105
	$\text{CH}_2=\text{CHOCOCCH}_3$	—	$\text{CHCl}_2\text{CH}_2\text{CHBrOCOCCH}_3$	—	105
CHBr_2	$\text{CH}_2=\text{CHC}_6\text{H}_{13}{}^n$	Ac_2O_2	$\text{CHBr}_2\text{CH}_2\text{CHBrC}_6\text{H}_{13}{}^n$	31	34
	$\text{CH}_2=\text{CHC}_6\text{H}_6$	Bz_2O_2	$\text{CHBr}_2\text{CH}_2\text{CHBrC}_6\text{H}_6$	10	34
CHI_3	$\text{CH}_2=\text{CHCH}_2\text{OCOC}_6\text{H}_5$	Ac_2O_2	$\text{CHI}_2\text{CH}_2\text{CHICH}_2\text{OCOC}_6\text{H}_5$	—	106
	Limonene	Ac_2O_2	$\begin{array}{c} \text{CHI}_2 \\ \\ \text{Cyclohexene ring} \\ \\ \text{IOCH}_2\text{CHI}_2 \\ \\ \text{CHI}_2 \end{array}$	35	106
CCl_4I	$\text{CH}_2=\text{CHCF}_3$	$h\nu$	$\text{OCCl}_2\text{CH}_2\text{CHICF}_3$	57	107
	$\text{CH}\equiv\text{CCF}_3$	$h\nu$	$\text{OCCl}_2\text{CH}=\text{CHCF}_3$	74	107


Note: References 35 to 160 are on pp. 147-149.

TABLE VIII—Continued
ADDITION OF OTHER POLYHALOALKANES

Polyhaloalkane	Unsaturated Compound	Initiator	Product(s)	Yield, %	Refs.
CF_2Br_2	$\text{CH}_2=\text{CH}_2$	Bz_2O_2	$\text{CF}_2\text{BrCH}_2\text{CH}_2\text{Br}$	34	108
	$\text{CH}_2=\text{CHF}$	Bz_2O_2	$\text{CF}_2\text{BrCH}_2\text{CHFBr}$	28	109
	$\text{CH}_2=\text{CF}_2$	Bz_2O_2	$\text{CF}_2\text{BrCH}_2\text{CF}_2\text{Br}$	9	109
	$\text{CHF}=\text{CF}_2$	Bz_2O_2	$\text{CF}_2\text{BrCHFCF}_2\text{Br}$	—	110
CCl_3Br_2	$\text{CH}_2=\text{CHCH}_3$	Bz_2O_2	$\text{CF}_2\text{BrCH}_2\text{CHBrCH}_3$	—	108
	$\text{CHF}=\text{CHCH}_3$	Bz_2O_2	$\text{CF}_2\text{BrCHFCBrCH}_3$	55	109
	$\text{CH}_3\text{CH}=\text{CHCH}_3$	Bz_2O_2	$\text{CF}_2\text{BrCH}(\text{CH}_3)\text{CHBrCH}_3$	—	108
	$\text{CH}_3\text{CH}=\text{CFCH}_3$	Bz_2O_2	$\text{CF}_2\text{BrCH}(\text{CH}_3)\text{CFBrCH}_3$	—	109
	$\text{CH}_2=\text{CHCH}_2\text{OC}_2\text{H}_5$	Bz_2O_2	$\text{CF}_2\text{BrCH}_2\text{CHBrCH}_2\text{OC}_2\text{H}_5$	31	75
	$\text{CH}_2=\text{CHCH}_2\text{OCF}_2\text{CHFCI}$	Bz_2O_2	$\text{CF}_2\text{BrCH}_2\text{CHBrCH}_2\text{OCF}_2\text{CHFCI}$	46	75
	$\text{CH}_2=\text{CHCH}_3$	—	$\text{CCl}_3\text{BrCH}_2\text{CHBrCH}_3$	—	105
	$\text{CH}_2=\text{C}(\text{CH}_3)_2$	—	$\text{CCl}_3\text{BrCH}_2\text{CBr}(\text{CH}_3)_2$	—	105
	$\text{CH}_2=\text{CH}_2$	$h\nu$ or Ac_2O_2	$\text{CBr}_3\text{CH}_2\text{CH}_2\text{Br}$	—	34
	$\text{CH}_2=\text{CHC}_6\text{H}_{13-n}$	$h\nu$ or Ac_2O_2	$\text{CBr}_3\text{CH}_2\text{CHBrC}_6\text{H}_{13-n}$	96	34
$\text{CH}_3\text{CCl}_2\text{Br}$ $\text{CF}_2=\text{CHI}$	$\text{CH}_2=\text{CHC}_6\text{H}_5$	$h\nu$	$\text{CBr}_3\text{CH}_2\text{CHBrC}_6\text{H}_5$	96	34
	$\text{CH}_2=\text{CHSi}(\text{Cl}_2)\text{CH}_3$	$h\nu$	$\text{CBr}_3\text{CH}_2\text{CHBrSiCl}_2\text{CH}_3$	—	83
	$\text{CH}_2=\text{CH}_2$	Bz_2O_2	$\text{CH}_3\text{CCl}_2\text{CH}_2\text{CH}_2\text{Br}$	(High)	110
	$\text{CH}_2=\text{CH}_2$	$h\nu$	$\text{CF}_2=\text{CHCH}_2\text{CH}_2\text{I}$	—	111
	$\text{CH}_2=\text{CF}_2$	$h\nu$	$\text{CF}_2=\text{CHCH}_2\text{CF}_2\text{I}$	—	111
	$\text{CF}_2=\text{CFCl}$	$h\nu$	$\text{CF}_2=\text{CHCF}_2\text{CFCl}$	—	111
	$\text{CH}_2=\text{CH}_2$	$h\nu$	$\text{CF}_2=\text{CFCH}_2\text{CH}_2\text{I}$	67	112
	$\text{CH}_2=\text{CHF}$	$h\nu$	$\text{CF}_2=\text{CFCH}_2\text{CHF}$	50	112
	$\text{CH}_2=\text{CF}_2$	$h\nu$	$\text{CF}_2=\text{CFCH}_2\text{CF}_2\text{I}$	24	112
	$\text{CF}_2=\text{CFI}$	$h\nu$	$\text{CF}_2=\text{CFCH}_2\text{CFI}_2$	50	112
$\text{CF}_2=\text{CFI}$	$\text{CF}_2=\text{CHCl}$	$h\nu$	$\text{CF}_2=\text{CFCH}_2\text{CF}_2\text{I}$	4	112
	$\text{CH}_2=\text{CH}_2$	$h\nu$	$\text{CF}_2=\text{CClCH}_2\text{CH}_2\text{I}$	—	111
	$\text{CH}_2=\text{CH}_2$	DTBP	$\text{CCl}_2=\text{CClCH}_2\text{CH}_2\text{Cl}$	—	113



TABLE IX
ADDITION OF ALDEHYDES

Aldehyde	Unsaturated Compound	Initiator	Product	Yield, % Telomers	Refs. 116-118 119
Acetaldehyde	Ethylene	Per.	$\text{CH}_3\text{COC}_2\text{H}_5$	—	116-118
	Acetylene	Per.	$\text{CH}_3=\text{CHCOCH}_3$	—	119
	Propylene	Per. or γ	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$	11	120, 118
	cis-2-Butene	γ	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$	—	118
	trans-2-Butene	γ	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{C}_2\text{H}_5$	—	118
	Isobutylene	γ	$\text{CH}_3\text{COCH}(\text{CH}_3)\text{C}_2\text{H}_5$	—	118
	1,5-Hexadiene	Per.	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CH}_3)_2$	15	120
	1-Octene	Per.	$\text{CH}_3\text{CO}(\text{CH}_2)_4\text{CH}=\text{CH}_2$	36	120
	1-Decene	Per.	$\text{CH}_3\text{COC}_8\text{H}_{17-n}$	36	120
	1-Dodecene	Per.	$\text{CH}_3\text{COC}_{10}\text{H}_{21-n}$	23	117, 120
Propionaldehyde	Allyl acetate	Per.	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{OCOCCH}_3$	63	121
	Acrolein diethyl acetal	Per.	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}(\text{OC}_2\text{H}_5)_2$	48	122
	Diethyl malate	Per.	$\text{CH}_3\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	78	123
	Methyl undecylenate	Per.	$\text{CH}_3\text{CO}(\text{CH}_2)_{10}\text{CO}_2\text{CH}_3$	30	124
	Mesityl oxide	Per.	$\text{CH}_3\text{CO}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$	31	125
	Perfluoropropylene	Per.	$\text{CH}_3\text{COCF}_2\text{CFHCF}_3$	76	126
	Ethylene	γ	$\text{C}_3\text{H}_5\text{COC}_2\text{H}_5$	—	118

n-Butyraldehyde	Ethylene	Per.	$n\text{-C}_3\text{H}_7\text{COC}_2\text{H}_5$	Telomers	116
Isobutyraldehyde	Isobutylene	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}_2\text{CH}(\text{CH}_3)_2$	30	120
1-Hexene	1-Hexene	Per.	$n\text{-C}_3\text{H}_7\text{COC}_4\text{H}_{13-n}$	41	127
Cyclohexene	Cyclohexene	Per.		Low	120
1-Octene	1-Octene	Per.	$n\text{-C}_3\text{H}_7\text{COC}_5\text{H}_{17-n}$	57	127
1-Dodecene	1-Dodecene	Per.	$n\text{-C}_3\text{H}_7\text{COC}_{12}\text{H}_{31-n}$	—	117
Acrolein diethyl acetal	Acrolein diethyl acetal	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}_2\text{CH}_2\text{CH}(\text{OC}_2\text{H}_5)_2$	24	121
Methyl acrylate	Methyl acrylate	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	11	124
Allyl acetate	Allyl acetate	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}_2\text{CH}_2\text{CH}_2\text{OCOCCH}_3$	63	121
Diethyl malate	Diethyl malate	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	70	123, 124
Dimethyl fumarate	Dimethyl fumarate	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	26	123, 124
3-Penten-2 one	3-Penten-2 one	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}(\text{CH}_3)\text{CH}_2\text{COCH}_3$	64	125
Methyl isopropenyl ketone	Methyl isopropenyl ketone	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}_2\text{CH}(\text{CH}_3)\text{COCH}_3$	—	128
5-Hexen 2-one	5-Hexen 2-one	Per.	$n\text{-C}_3\text{H}_7\text{CO}(\text{CH}_3)_2\text{COCH}_3$	71	128
Mesityl oxide	Mesityl oxide	Per.	$n\text{-C}_3\text{H}_7\text{COC}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$	60-100	125
Phorone	Phorone	Per.	$n\text{-C}_3\text{H}_7\text{COC}(\text{CH}_3)_2\text{CH}_2\text{COCH}=\text{C}(\text{CH}_3)_2$	80	125
3-Decen-2 one	3-Decen-2 one	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}(\text{C}_4\text{H}_9)\text{CH}_2\text{COCH}_3$	42	125
Crotonophenone	Crotonophenone	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}(\text{CH}_3)\text{CH}_2\text{COC}_6\text{H}_5$	24	125
3,3-Diphenyl-1-buten	3,3-Diphenyl-1-buten	Per.	$n\text{-C}_3\text{H}_7\text{COCCH}(\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2$	—	15
Perfluoropropylene	Perfluoropropylene	Per.	$n\text{-C}_3\text{H}_7\text{COCF}_2\text{CHF}_2$	70	126

Note. References 35 to 160 are on pp. 147-149.

TABLE IX—Continued

ADDITION OF ALDEHYDES					
Aldehyde	Unsaturated Compound	Initiator	Product	Yield, %	Refs.
Isobutyraldehyde	Ethylene	γ	$(\text{CH}_3)_3\text{CHCO}_2\text{C}_2\text{H}_5$	—	118
	1-Octene	Per.	$(\text{CH}_3)_3\text{CHCO}_2\text{C}_8\text{H}_{17}{}^n$	Low	120
Trimethyl-acetaldehyde	Ethylene	γ	$(\text{CH}_3)_3\text{CCOC}_2\text{H}_5$	—	118
<i>n</i> -Heptanal	1-Octene	Per.	$n\text{-C}_6\text{H}_{13}\text{COC}_8\text{H}_{17}{}^n$	75	127
	Cyclohexene	Per.	 $\text{COC}_6\text{H}_{13}{}^n$	Low	127
	Vinyl cyclohexene	Per.	 $\text{CH}_3\text{CH}_2\text{COC}_6\text{H}_{13}{}^n$	21	120
	Mesityl oxide	Per.	$n\text{-C}_6\text{H}_{13}\text{COC}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$	61	125
	Dioethyl malate	Per.	$n\text{-C}_6\text{H}_{13}\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	76	123
2- <i>n</i> -Propyl-pentanal	Dioethyl malate	Per.	$(n\text{-C}_3\text{H}_7)_2\text{CHCOCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	59	123
β -Methoxy-propionaldehyde	Dioethyl malate	Per.	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	55	123
Glutaraldehyde	Dioethyl malate	Per.	$\text{CH}_2[\text{CH}_2\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5]_2$	100	123
Benzaldehyde	Dioethyl malate	Per.	$\text{C}_6\text{H}_5\text{COCH}(\text{CO}_2\text{C}_2\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$	5	123






Note: References 35 to 160 are on pp. 147–149.

TABLE X—Continued
ADDITION OF ALCOHOLS

Alcohol	Unsaturated Compound	Initiator	Product	Yield, %	Refs.
Cyclohexanol (cont.)	1-Octeno	DTBP		—	29
	Acrylic acid	DTBP		—	129
	1-Hexeno	DTBP	$(n\text{-C}_6\text{H}_{13})_2\text{CHOH}$	—	128
1-Heptanol	Acrylic acid	DTBP		—	129
	Methyl acrylate	DTBP	$n\text{-C}_6\text{H}_{13}$	—	129
	1-Hexeno	DTBP	$n\text{-C}_6\text{H}_{13}\text{CHOHC}_7\text{H}_{15}\text{-}\eta$	—	128
1-Octanol	1-Hepteno	DTBP	$(n\text{-C}_7\text{H}_{15})_2\text{CHOH}$	—	128
	1-Noneno	DTBP	$n\text{-C}_9\text{H}_{19}\text{CHOHC}_7\text{H}_{15}\text{-}\eta$	—	128
	Acrylic acid	DTBP		—	129
2-Ethyl-1-hexanol	Acrylic acid	DTBP	$n\text{-C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)$	—	129
	1-Hexeno	DTBP	$n\text{-C}_6\text{H}_{13}\text{CHOHC}_8\text{H}_{17}\text{-}\eta$	—	128
	1-Hepteno	DTBP	$n\text{-C}_7\text{H}_{15}\text{CHOHC}_8\text{H}_{17}\text{-}\eta$	—	128
1-Nonanol	Methyl acrylate	DTBP	$n\text{-C}_8\text{H}_{17}$	—	129
	1-Hexeno	DTBP	$n\text{-C}_8\text{H}_{17}\text{CHOHC}_6\text{H}_{13}\text{-}\eta$	—	128
	1-Hepteno	DTBP	$n\text{-C}_9\text{H}_{19}\text{CHOHC}_6\text{H}_{13}\text{-}\eta$	—	128
1-Decanol	Methyl acrylate	DTBP	$n\text{-C}_9\text{H}_{19}$	—	129
	1-Hexeno	DTBP	$n\text{-C}_9\text{H}_{19}\text{CHOHC}_6\text{H}_{13}\text{-}\eta$	—	128



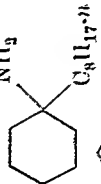
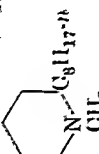
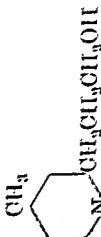
Note: References 35 to 160 are on pp. 147-149.

TABLE XI
ADDITION OF AMINES


Amine	Unsaturated Compound	Initiator	Product	Yield, %	Refs.
Isopropylamine	1-Octene	DTBP	$(CH_3)_2C(NH_2)C_6H_{13-n}$	46	130
n-Butylamine	1-Octene	DTBP, A_v	$n-C_3H_7CH(NH_2)C_6H_{13-n}$	36	130
Pyrrolidine	Allyl alcohol	DTBP		63	130
Piperidine	Ethylene	DTBP		—	130
	Propylene	DTBP		—	130, 131
	1-Hexene	DTBP		60	130
	1-Octene	DTBP, A_v		70	130, 131

Note: References 35 to 160 are on pp. 147-149.

TABLE XI—Continued

Amine	Unsaturated Compound	ADDITION OF AMINES		Yield, %	Refs.
		Initiator	Product		
Piperidine (<i>cont.</i>)	Allyl alcohol	DTBP		54	130
	Allyl cyanide	DTBP		48	130
n-Hexylamine	1-Octene	DTBP	$n\text{-C}_6\text{H}_{11}\text{CH}(\text{NH}_2)\text{C}_8\text{H}_{17}$	36	130
Cyclohexylamine	1-Octene	DTBP		55	130
N-Methylpiperidine	1-Octene	DTBP		22	130
γ-Pipecoline	Allyl alcohol	DTBP		42	130

Note: References 35 to 160 are on pp. 147–149.







TABLE XII				
ADDITION OF FORMIC ACID DERIVATIVES				
Addend	Unsaturated Compound	Initiator	Product(s)	Yield, % Telomers Telomers Refs.
Methyl formate	Ethylene	DTBP	$C_2H_5CO_2CH_3$	132, 133
	Propylene	DTBP	$n-C_3H_7CO_2CH_3$	133
	1-Hexene	DTBP	$n-C_6H_{13}CO_2CH_3$	132
	Cyclohexene	DTBP		134
Ethyl formate	1-Octene	DTBP	$n-C_8H_{17}CO_2CH_3$	134
	1-Decene	DTBP	$n-C_{10}H_{21}CO_2CH_3$	134
	1-Dodecene	DTBP	$n-C_{12}H_{25}CO_2CH_3$	134
	Ethylene	DTBP	$C_2H_5CO_2C_2H_5$ and $HCO_2CH(C_2H_5)CH_3$	132
N,N-Dimethyl- formamide	1-Octene	DTBP	$n-C_8H_{17}CON(CH_3)_2$	135
	1-Octene	DTBP	$HCON(CH_3)C_8H_{17}$	135
	Methyl 10-undecylenate	DTBP	$n-C_{11}H_{23}CONHCO(CH_2)_2CH_3$ $CH_3O_2C(CH_2)_{10}CONHC(CH_2)_3$	135 135

Note. References 35 to 160 are on pp. 147-149.

$\text{CH}_3\text{CH}_2\text{CH}_2$ O—CO	1-Octene	DTBP	$\text{CH}_3\text{CH}_2\text{CHCH}_2\text{C}_6\text{H}_{13}$ O—CO	61	30
$\text{C}_6\text{H}_5\text{CH}(\text{CO}_2\text{C}_6\text{H}_5)_2$	1-Hexene	DTBP	$n\text{-C}_7\text{H}_{15}\text{C}(\text{C}_6\text{H}_5)(\text{CO}_2\text{C}_6\text{H}_5)_2$	74	30
	1-Octene	DTBP	$n\text{-C}_9\text{H}_{17}\text{C}(\text{C}_6\text{H}_5)(\text{CO}_2\text{C}_6\text{H}_5)_2$	60	134
$\text{CH}_2\text{CHCH}_2\text{CH}_3$ O—CO	1-Octene	DTBP	$\text{CH}_2\text{CHCH}_2\text{CHCH}_2\text{C}_6\text{H}_{13}$ O—CO	62	30
$\text{Cl}_3\text{CCHCO}_2\text{CH}_3$ B-CHCO_2CH_3 CH_2CO_2CH_3	1-Octene	DTBP	$\text{Cl}_3\text{CCHCO}_2\text{CH}_3$ $n\text{-C}_6\text{H}_{13}\text{CH}=\text{CHCHCO}_2\text{CH}_3$ $n\text{-C}_7\text{H}_{15}\text{CHCO}_2\text{CH}_3$	80	82
CH_3 $\text{CH}_2\text{CO}_2\text{CH}_3$	1-Octene	DTBP	CH_3 $\text{CH}_2\text{CO}_2\text{CH}_3$ $n\text{-C}_{11}\text{H}_{23}\text{CHCO}_2\text{CH}_3$	42	139
	1-Decene	DTBP	CH_3 $\text{CH}_2\text{CO}_2\text{CH}_3$ $n\text{-C}_2\text{H}_5\text{CHCO}_2\text{CH}_3$	38	139
$\text{CH}_2\text{CO}_2\text{CH}_3$ $(\text{CH}_2)_4$ $\text{CH}_2\text{CO}_2\text{CH}_3$ $\text{CH}_2\text{CO}_2\text{CH}_3$	1-Octene	DTBP	$n\text{-C}_2\text{H}_5\text{CHCO}_2\text{CH}_3$ $(\text{CH}_2)_3$ $\text{CH}_2\text{CO}_2\text{CH}_3$ $n\text{-C}_8\text{H}_{17}\text{CHCO}_2\text{CH}_3$	52	139
$(\text{CH}_2)_4$ $\text{CH}_2\text{CO}_2\text{CH}_3$	1-Octene	DTBP	$(\text{CH}_2)_4$ $\text{CH}_2\text{CO}_2\text{CH}_3$	55	139

Note: References 35 to 160 are on pp. 147-149.

TABLE XIV

ADDITION OF ETHERS AND ACETALS			Yield, %	Refs.
Addend	Unsaturated Compound	Initiator Product		
$(C_2H_5)_2O$ ($\frac{1}{2}$ $C_2H_5)_2O$ $(CH_3OCH_2)_4$ $CH_3(OCH_2)_2$	Perfluoroethylene	Bz_2O_2 Product: $C_2H_5OCH(CH_2CF_2)CH_2CF_2$	—	143
	1-Octene	$DTBP$ Product: $n-C_8H_{17}OCH(C_2H_5)_2$	—	144
	Perfluoroethylene	Bz_2O_2 Product: $C_2H_5OCH_2CF_2$	—	143
	Perfluoroethylene	Bz_2O_2 Product: $C_2H_5OCH_2CF_2$	Telomers	143
Maleic anhydride		$(CH_3O)_2CHCH=CO$ 	36	145
$CH_3(OC_2H_5)_2$	Dimethyl maleate	Bz_2O_2 or $h\nu$ Product: $C_2H_5OCH_2OCH(CH_2CHCO_2CH_3)_2$	—	146
$CH_3(OC_2H_5)_{1-n}$	Dimethyl maleate	Bz_2O_2 Product: $(n-C_2H_5O)_nCHCHCO_2CH_3$ 	—	147
$CH_3CH(OC_2H_5)_2$	Dimethyl maleate	Bz_2O_2 Product: $(C_2H_5O)_2C(CH_2)CHCO_2CH_3$ 	—	147
	Diethyl maleate	— Product: $(C_2H_5O)_2C(CH_2)CHCO_2C_2H_5$ 	—	148
	Diethyl fumarate	— Product: $(C_2H_5O)_2C(CH_2)CHCO_2C_2H_5$ 	—	148
	Di-2-ethylhexyl maleate	— Product: $(C_2H_5O)_2C(CH_2)CHCO_2CH_2CH(C_2H_5)_2$ 	—	148

Note: References 35 to 160 are on pp. 147-149.

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CHAPTER 4

FORMATION OF CARBON-HETERO ATOM BONDS BY FREE RADICAL CHAIN ADDITIONS TO CARBON-CARBON MULTIPLE BONDS

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INTRODUCTION

Free radical chain addition to carbon-carbon multiple bonds to form carbon-hetero atom bonds is an important synthetic method of wide scope. Carbon-halogen, carbon-sulfur, carbon-silicon, carbon-germanium, carbon-phosphorus, and carbon-nitrogen bonds have been formed by this method. In this chapter, the mechanism, scope, limitations, and experimental conditions are treated for the addition reactions that lead to the

formation of the six types of carbon-hetero atom bonds mentioned above * However, since the direction of addition of free radicals to carbon-carbon multiple bonds is common to all the classes reviewed, it is taken up briefly first

In general, experimental procedures for carrying out free radical additions are similar irrespective of the addendum, hence, we have chosen to collect representative experimental procedures at the end of the discussion rather than to include them with the discussions of the classes to which they belong

A theoretical treatment of free radical addition reactions, generally, has been given by Walling and Huiser in Chapter 3 of this volume

ORIENTATION IN FREE RADICAL ADDITIONS

Historically, the orientation in free radical additions of HX compounds to unsymmetrically substituted olefins has been termed anti Markownikoff or abnormal from the relation of the products to those obtained by ionic addition. Thus the free radical chain addition of hydrogen bromide to propylene gives *n*-propyl bromide, whereas ionic addition gives isopropyl bromide Present evidence indicates that the orientation in free radical additions can be most generally correlated by considering the relative stabilities of the intermediate radicals that can be formed in the addition step and assuming that the product derives from the more stable radical. The prediction of relative radical stabilities is based on the premise that radicals have the following order of decreasing stability: tertiary > secondary > primary. For example, in the addition of hydrogen bromide to propylene, the chain-carrying bromine atom could add to give either 1 or 2 as the intermediate radical. The secondary radical 1 would be the



more stable in this instance and the product of the reaction would be *n*-propyl bromide, as observed. In their broadest sense, the designations primary, secondary, and tertiary are determined solely by the number of

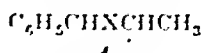
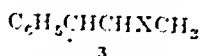
* In addition to these rather extensively studied types, there are scattered reports of the formation of carbon-selenium,¹ carbon-oxygen,² and carbon-tin³ bonds by free radical chain addition processes.

¹ Volger and Arena, *Rec. Trav. Chim.*, **77**, 1170 (1958).

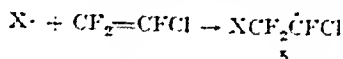
² (a) Gray and Williams, *Chem. Rev.*, **59**, 272 (1959). (b) Allison and Caley, *J. Am. Chem. Soc.*, **81**, 1089 (1959). (c) Russell, *ibid.*, **78**, 1035 (1956). (d) Kharasch, Arimoto, and Nudenberg, *J. Org. Chem.*, **18**, 1559 (1951).

³ (a) Smolin, *Tetrahedron Letters*, **1961**, 142. (b) Berg and Clark, *Chem. & Ind. (London)*, **1962**, 140. (c) Neumann, *Angew. Chem., Intern. Ed. Engl.*, **2**, 170 (1963).

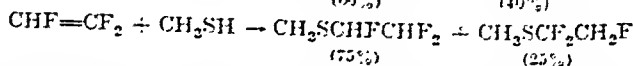
atoms or groups other than hydrogen on the carbon atom bearing the odd electron, without reference to the carbon skeleton of the radical. Of course, substituents differ in their stabilizing ability so that two radicals of equal multiplicity may differ widely in stability, and a given primary or secondary radical may actually be more stable than a particular secondary or tertiary one. For example, in additions to β -methylstyrene the intermediate benzyl radical 3 is stabilized by resonance and thus much preferred to the alternative intermediate 4. Accordingly, the radical, $\cdot X$,



always goes to the β -carbon atom of the double bond. From studies of radical additions to a group of fluoroolefins the following order of radical stabilizing ability has been derived: $\text{H} < \text{F} < \text{Cl}$.⁴ Thus in additions to chlorotrifluoroethylene, radicals attack at CF_2 rather than at CFCl to give the intermediate radical 5. In radical additions of hydrogen bromide⁵ and methyl mercaptan⁶ to trifluoroethylene, both possible adducts are



formed, suggesting rather small differences, if any, in the relative stabilities



of the intermediate radicals. Other instances are known wherein both possible isomers are formed by the free radical addition. They are discussed in the appropriate sections.

It has been stated⁷ that polar and steric factors play little or no part in determining the orientation of radical additions, but recent studies⁶ suggest that electronic (polar) factors may play an important role in certain cases, such as those wherein the stabilities of the alternative intermediate radicals do not differ greatly. Be that as it may, the direction of radical attack can generally be predicted by considering only the relative stabilities of the alternative intermediate radicals.

FREE RADICAL HYDROHALOGENATIONS

The free radical chain addition of hydrogen halides to unsaturates is a convenient and important method for the synthesis of a variety of alkyl

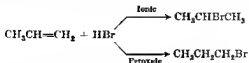
⁴ Hazeldine and Steele, *J. Chem. Soc.*, 1957, 2193.

⁵ Hazeldine and Steele, *J. Chem. Soc.*, 1957, 2599.

⁶ Harris and Stacey, *J. Am. Chem. Soc.*, 83, 849 (1961).

⁷ Hazeldine, *J. Chem. Soc.*, 1953, 3561.

and alkenyl halides. Its use as a synthetic procedure is restricted mainly to hydrogen bromide, though a few examples of hydrogen chloride additions are known. The products of the free radical addition are generally isomers of those obtained by the corresponding normal or ionic reaction. Thus propylene gives only isopropyl bromide under ionic conditions, but *n*-propyl bromide under radical conditions. Exceptions



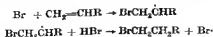
to this rule occur with certain internal olefins where a 50:50 mixture of isomers is frequently formed by either ionic or radical addition, and with α,β -unsaturated carbonyl compounds where the same product is generally obtained under all conditions. Radical chain additions have not been unequivocally established with the latter compounds, although they probably occur.

This discussion and accompanying tables are concerned with reactions the radical nature of which has been established or is highly probable. Omitted for the most part are those instances where the same product or mixture of products results irrespective of the conditions used. An excellent discussion of the historical aspects of the peroxide effect and of the published results on hydrohalogenation up to 1940 is contained in a review article by Mayo and Walling.⁸

Mechanism

The most satisfactory mechanism for the abnormal or anti-Markownikoff addition of hydrogen bromide to olefins is the free radical chain process involving bromine atoms as the chain-carrying species first proposed by Kharasch and co-workers⁹ and by Hey and Waters.¹⁰

The steps in the chain propagation are shown. The reaction has



not been investigated from a kinetic viewpoint, but it shows all the usual characteristics associated with radical chain processes. It is initiated by

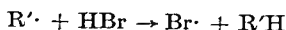
⁸ Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

⁹ Kharasch, Engelsmann, and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

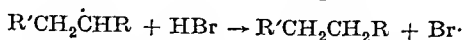
¹⁰ Hey and Waters, *Chem. Rev.*, **21**, 189 (1937).

light,¹¹ by peroxides,¹² and by other radical generating systems;^{13,14} it is inhibited by antioxidants such as hydroquinone and diphenylamine, and it is relatively independent of the polar nature of the solvent.

Initiation of the reaction by peroxides or other radical-producing initiators probably occurs through attack of the initiating radicals (R') on hydrogen bromide. However, primary attack of initiator radicals on



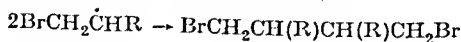
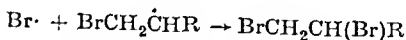
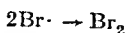
the olefin, followed by transfer with hydrogen bromide cannot be ruled out. Initiation by ultraviolet irradiation in the absence of photosensi-



tizers occurs only in the region below about 2900 Å, where hydrogen bromide absorbs. Under these conditions the initiation step must be a homolytic cleavage of the hydrogen bromide.¹¹

Freshly reduced iron, nickel, and cobalt have been shown to catalyze the additions to allyl bromide^{15,16} and to undecenoic acid.^{17,18} It seems probable that their effectiveness as initiators is associated with an ability to generate bromine atoms from hydrogen bromide.¹⁹ Molecular oxygen apparently behaves as an initiator, per se, and not necessarily through the intermediacy of peroxidation of the olefin.¹⁹⁻²¹

Chain termination can occur by any of the following processes.



In general, the chains are long, and detectable amounts of the chain-termination products are seldom found. With the single exception of

¹¹ Vaughan, Rust, and Evans, *J. Org. Chem.*, **7**, 477 (1942).

¹² Kharasch and Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).

¹³ Rust and Vaughan, U.S. pat. 2,299,411 [*C.A.*, **37**, 1722 (1943)].

¹⁴ Bataafsche Pet. Maatschappij, Brit. pat. 668,159 [*C.A.*, **48**, 7914 (1952)].

¹⁵ Kharasch and Potts, *J. Org. Chem.*, **2**, 195 (1937).

¹⁶ Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **12**, 51 (1937); **13**, 400 (1938) [*C.A.*, **31**, 3867 (1937); **32**, 7014 (1938)].

¹⁷ Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **13**, 331, 404, 574 (1938) [*C.A.*, **32**, 4944, 7015 (1938); **33**, 132 (1939)].

¹⁸ Takebayashi, *Bull. Chem. Soc. Japan*, **15**, 113, 116 (1940) [*C.A.*, **34**, 5824 (1940)].

¹⁹ Urushibara, *J. Chem. Soc. Japan*, **60**, 717 (1939) [*C.A.*, **36**, 6135 (1942)].

²⁰ Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **11**, 798 (1936); **12**, 138 (1937) [*C.A.*, **31**, 2164, 4641 (1937)].

²¹ Urushibara and Sitanamura, *Bull. Chem. Soc. Japan*, **14**, 323 (1939) [*C.A.*, **34**, 367 (1940)].

vinylidene chloride, which is said to give a 2:1 adduct,²² there is no report of the formation of telomers of the type $\text{Br}(\text{CH}_2\text{CHR})_n\text{H}$ ($n > 1$). This fact attests to the great efficiency of hydrogen bromide as a transfer agent.

Recently attention has been directed to the steric aspects of free radical additions of hydrogen bromide to olefins and acetylenes. Stereospecific *trans* additions have been noted with both cyclic and acyclic olefins under appropriate conditions. Thus the additions of deuterium bromide to *cis*- and *trans*-2-butene at -60° to -78° give essentially pure ($<1\%$ isomer intercontamination) *threo*- and *erythro*-3-deutero-2-bromobutane, respectively.²³ Additions of hydrogen bromide and deuterium bromide to *cis*- and *trans*-2-bromo-2-butene are stereospecific at -80° in a large excess of the liquid halide.²⁴ The stereoselectivity decreases with decreasing hydrogen bromide/olefin ratio and with increasing reaction temperature so that at 25° the same mixture of 75% *dl*- and 25% *meso*-2,3-dibromobutane is obtained from either *cis*- or *trans*-2-bromo-2-butene. Both *cis*- and *trans*-2-chloro-2-butene are rapidly equilibrated by hydrogen bromide to a mixture containing 80% *trans* and 20% *cis*, even at -78° . From either pure *cis*- or pure *trans*-olefin, the adduct consists of a mixture of 70% *threo*- and 30% *erythro*-2-bromo-3-chlorobutane.²⁵ Comparison of the product composition with that of the equilibrium mixture of olefin isomers (equilibration having occurred prior to addition) shows that *trans* addition predominates here also.

Additions to 1-chloro-, 1-bromo-, and 1-methyl-cyclohexene occur with high stereoselectivity to yield *cis*-1-bromo-2-chlorocyclohexane, *cis*-1,2-dibromocyclohexane, and *cis*-1-bromo-2-methylcyclohexane, respectively.^{26,27} Less than 1% of the *trans* isomer is formed with 1-bromocyclohexene. However, in comparable additions to 1-bromocyclobutene, 1-bromocyclopentene, and 1-bromocycloheptene, the degree of stereoselectivity is lower. The ratios of *cis*:*trans* adducts in these cases are 79:21, 94:6, and 91:9, respectively.²⁸ The difference in stereoselectivity with ring size has been attributed to a balance between the mechanistic preference for *trans* addition and the degree of steric inhibition to formation of the *cis* adducts.²⁸ An interesting case is the hydrobromination of 2-bromo-2-norbornene from which the principal products are *trans* 2,3-dibromonorbornane (6) and *exo cis*-2,3-dibromonorbornane (7), in a ratio

²² Francis and Leitch, *Can. J. Chem.*, **35**, 500, (1957).

²³ Skell and Allen, *J. Am. Chem. Soc.*, **81**, 5383 (1959).

²⁴ Goering and Larsen, *J. Am. Chem. Soc.*, **81**, 5937 (1959).

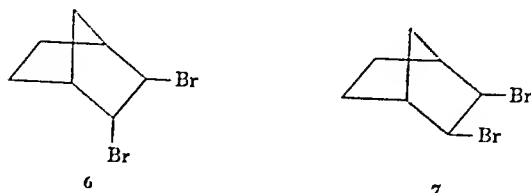
²⁵ Neuretter and Bordwell, *J. Am. Chem. Soc.*, **82**, 5354 (1960).

²⁶ Goering, Abell, and Aycock, *J. Am. Chem. Soc.*, **74**, 2588 (1952).

²⁷ Goering and Sims, *J. Am. Chem. Soc.*, **77**, 3465 (1955).

²⁸ Abell and Chiao, *J. Am. Chem. Soc.*, **82**, 3610 (1960).

of about 5:2.²⁹ The formation of both of these products can be explained by an initial *exo* attack of a bromine atom followed by transfer with



hydrogen bromide. The major product derives from transfer from the less sterically hindered *exo* side and is formally then a *cis* addition. Adduct 7, on the other hand, derives from the usually dominant *trans* addition, inhibited in the present case by the steric factor.

Both *cis* and *trans* additions to acetylenes have been reported. Propyne gives solely *cis*-1-bromo-1-propene when irradiated in the liquid phase at -60° to -78° .³⁰ In the gas phase, rapid equilibration of the product prevented determination of the degree of stereoselectivity. The formation of *dl*-2,3-dibromobutane by addition of hydrogen bromide to 2-butyne³¹ almost certainly involves two consecutive stereospecific *trans* additions, although this was not recognized at the time the work was done. Additions to 1-bromopropyne and to 1-bromo-3,3-dimethyl-1-butyne have been reported to yield predominantly *trans*-1,2-dibromopropene and *trans*-1,2-dibromo-3,3-dimethyl-1-butene, respectively, by *cis* additions.³² The addition of hydrogen bromide to phenylpropiolie acid in benzene solution forms *trans*- α -bromocinnamic acid in 95% yield.³³ The radical nature of this addition, although not proved, seems probable in view of the fact that catechol inhibits the formation of this product. Further studies appear to be required to elucidate the apparent differences in the stereochemistry of the additions to acetylenes.

The high degree of stereoselectivity observed in hydrogen bromide additions requires that the rate of the chain transfer step compete successfully with that of radical interconversion through rotation about a C—C bond or, in the case of cyclic compounds, with conformational isomerization. Several proposals have been put forward to rationalize the stereoselectivity and dominant *trans* addition. An intermediate with the bridged structure 8, together with contributing forms containing three-electron bonds, has been considered.²⁵ The possibility of existence of

²⁹ LeBel, *J. Am. Chem. Soc.*, **82**, 623 (1960).

³⁰ Skell and Allen, *J. Am. Chem. Soc.*, **80**, 5937 (1958).

³¹ Walling, Kharasch, and Mayo, *J. Am. Chem. Soc.*, **61**, 1711 (1939).

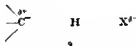
³² L. D. Bergelson, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, **1960**, 1145.

³³ Kasiwagi, *Bull. Chem. Soc. Japan*, **25**, 81 (1952); **31**, 985 (1958).

such an intermediate at low temperatures has been demonstrated by EPR studies.³⁴ However, the concept appears inadequate to explain some of the observations in hydrogen bromide additions.²⁹



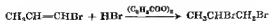
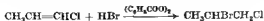
An alternative proposal envisions reaction between a bromine atom and an olefin hydrogen bromide complex^{24,27,30} as a means of rapid hydrogen atom transfer. Neureiter and Bordwell²⁵ have recently proposed a polar-steric scheme wherein the development in the transition state 9 of a dipole,



oriented away from the largest permanent (negative) dipole on the saturated carbon atom, causes the molecule undergoing transfer to approach the radical center *trans* to the most negative group on the saturated carbon atom.

Scope and Limitations

The radical addition of hydrogen bromide has been applied to a considerable variety of unsaturated compounds, including terminal olefins, halogenated ethylenes, internal (including cyclic) olefins, mono- and di-substituted acetylenes, vinylsilanes, etc. The reaction with terminal olefins is a very general one for the synthesis of the corresponding 1-bromoalkanes, although substitution of certain groups such as chlorine, bromine, or carboxyl on the terminal carbon atom of the double bond can direct the addition to yield the 2-bromo adduct as in the following examples³

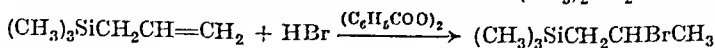
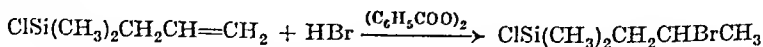


1-Bromo-1-hexene, which reacts only very slowly with hydrogen bromide in the presence of an antioxidant, gives a 75% yield of 1,2-dibromohexane in 15 hours at 10° in the presence of a trace of peroxide.³³

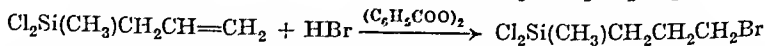
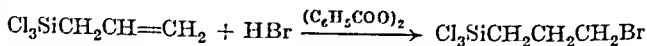
³⁴ Abell and Piette, *J. Am. Chem. Soc.*, **84**, 518 (1962)

³³ Young, Vogt, and Nieuwland, *J. Am. Chem. Soc.*, **53**, 1896 (1935)

The direction of addition to allylsilanes is remarkable in that some reactions lead to Markownikoff products even in the presence of peroxides.^{36,37}



However,



These observations might be considered manifestations of the predominance of ionic addition in certain reactions and of radical addition in others, but this seems unlikely in view of the fact that yields are high and mixtures of isomers are apparently not obtained.

Unequivocal evidence for radical chain addition to α,β -unsaturated acids and esters has not been presented, and it is reported in nearly all cases studied that the same products (the β -bromo acids or esters) are obtained in the presence or absence of peroxides or antioxidants.* This may mean that the ionic addition predominates under all conditions, but it is more likely that it merely indicates the operation of a directive influence of the terminal carboxyl or carbalkoxyl group in the radical addition process. As with terminal olefins, so also with monosubstituted acetylenes the 1:1 products are those deriving from attachment of the bromine atom to the terminal carbon atom.^{30,35,39,40} In the presence of excess hydrogen bromide, the alkenyl halides react further to give, in all cases, the 1,2-dibromoalkanes.^{30,35,41}

The orientation in additions of hydrogen bromide is generally that which would be predicted on the basis of intermediate radical stabilities. Thus propylene gives only *n*-propyl bromide and 1-chlorocyclohexene gives only 1-chloro-2-bromocyclohexane. However, the orientation with some fluoroolefins, is less clear cut. For example, 1,1-difluoropropene is reported to yield 2-bromo-1,1-difluoropropane;⁴² and trifluoroethylene gives a mixture of the two possible isomers, 1-bromo-1,2,2-trifluoro- and

³⁶ Sommer, Tyler, and Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948).

³⁷ Mironov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1959, 1781.

* The apparent lone exception is the addition to phenylpropionic acid, where the product in non-polar solvents under oxidant conditions is α -bromocinnamic acid.³³ The orientation of adduct in this case is that expected for radical addition, considering intermediate radical stabilities. The β -bromo adduct is obtained in polar solvents.³³

³⁸ Michael, *J. Org. Chem.*, **4**, 128 (1939).

³⁹ Haszeldine, *J. Chem. Soc.*, 1952, 3490.

⁴⁰ Harris and Smith, *J. Chem. Soc.*, 1935, 1572.

⁴¹ Kharasch, McNab, and McNab, *J. Am. Chem. Soc.*, **57**, 2463 (1935).

⁴² Haszeldine, *J. Chem. Soc.*, 1953, 3565.

1-bromo-1,1,2-trifluoro-ethane in a ratio of about 60:40, both formed by the radical chain mechanism.⁴³ Similarly, hexafluoropropene yields both possible isomers in the ultraviolet- or x-ray-induced reaction.⁴⁴

Free radical chain additions of hydrogen fluoride or of hydrogen iodide to olefins have never been observed. The energetics of the chain propagation steps for the addition of the various hydrogen halides to ethylene are shown in Table I.⁴⁵

The failure of hydrogen fluoride to add is undoubtedly due to the very high strength of the hydrogen-fluorine bond. The energetics for radical

TABLE I

H—X	ΔH (kcal /mole at 25°) $X\cdot + CH_2=CH_2$	ΔH (kcal /mole at 25°) $XCH_2CH_2\cdot + H-X$
H—F	—	37
H—Cl	-26	5
H—Br	-5	-11
H—I	7	-27

addition of hydrogen iodide indicate that attack of the iodine atom on the double bond should be slow. Another difficulty with the addition of hydrogen iodide is the catalysis of the ordinarily rapid ionic addition by iodine. Very few radical additions of hydrogen chloride to olefins have been demonstrated. Addition to ethylene has been observed to occur in the vapor phase under the influence of either ultraviolet radiation or radicals generated from di-*t*-butyl peroxide.⁴⁶ Only a very slow addition to propylene was observed under these conditions, and isobutylene proved to be an inhibitor for the ethylene addition. In the liquid phase, additions to *t*-butylethylene,⁴⁷ allyl chloride,⁴⁸ and propylene⁴⁸ have been reported, but in all cases the chain lengths are short and the major products obtained are those resulting from the competing ionic additions. Low telomers are also generally found, and, in fact, a whole series of even-numbered *n*-alkyl chlorides has been obtained by heating ethylene at high pressure (100–1000 atm.) with aqueous hydrochloric acid at 100° in the presence of benzoyl peroxide.⁴⁹ In general, the radical chain addition of hydrogen chloride to olefins is not a useful preparative method.

⁴³ Hazeldine and Steele, *J. Chem. Soc.*, 1957, 2800.

⁴⁴ Stacey and Harris, *J. Org. Chem.*, **27**, 4089 (1962).

⁴⁵ Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, 1957.

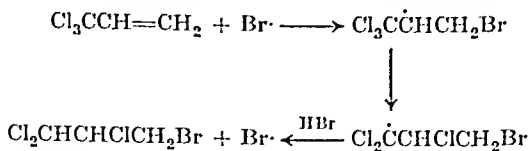
⁴⁶ Raley, Rust, and Vaughan, *J. Am. Chem. Soc.*, **70**, 2767 (1948).

⁴⁷ Leke, Cook, and Whitmore, *J. Am. Chem. Soc.*, **72**, 1511 (1950).

⁴⁸ Mayo, *J. Am. Chem. Soc.*, **76**, 5392 (1954).

⁴⁹ Ford, Hanford, Hermon, and Lipscomb, *J. Am. Chem. Soc.*, **74**, 4323 (1952).

Examples of radical rearrangement in hydrogen bromide additions have been reported by Nesmeyanov and his co-workers.⁵⁰⁻⁵³ The rearrangements all involve a 1,2 shift of a chlorine atom, as illustrated in the accompanying equation. The major product of addition to 3,3,3-trichloropropene is, accordingly, not 1,1,1-trichloro-3-bromopropene as



originally thought,⁵¹ but 1,1,2-trichloro-3-bromopropene.⁵⁰ Similarly, the olefins 3,3,3-trichloro-2-methylpropene, 2,3,3,3-tetrachloropropene, and 3,3-dichloro-1-butene add hydrogen bromide in the presence of peroxide to give the rearranged adducts 1-bromo-2,3,3-trichloro-2-methylpropane,⁵¹ 1-bromo-2,2,3,3-tetrachloropropene,⁵² and 1-bromo-2,3-dichlorobutane,⁵⁵ respectively, as the major products. By contrast, 2,3,3-trichloropropene gives the unrearranged adduct, 1-bromo-2,3,3-trichloropropane,⁵² while 3,3-dichloro-2-methylpropene,⁵⁵ 3,3-dichloropropene,^{55,56} and 3-fluoro-3,3-dichloropropene,⁵⁷ give mixtures of rearranged and unrearranged adducts.

Experimental Conditions

An important consideration in any attempt to prepare specific halides by the free radical addition of hydrogen bromide (or hydrogen chloride) to unsaturates is the relative rates of the competing ionic and radical additions. The rates of the uncatalyzed ionic addition vary markedly from one olefin to another. Consequently, the precautions required to avoid interference by the ionic addition vary widely. When the ionic addition is extremely slow, as with such olefins as 1-bromopropene⁹ or

⁵⁰ Nesmeyanov, Freidlina, and Zakharkin, *Doklady Akad. Nauk SSSR*, **81**, 199 (1951) [*C.A.*, **47**, 3789 (1953)].

⁵¹ Nesmeyanov, Freidlina et al., *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, **1959**, 992.

⁵² Freidlina, Kost, Khorlina, and Nesmeyanov, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **128**, 755 (1959).

⁵³ Nesmeyanov, Freidlina, Kost, and Khorlina, *Tetrahedron*, **16**, 94 (1961).

⁵⁴ Kharasch, Rossin, and Fields, *J. Am. Chem. Soc.*, **63**, 2558 (1941).

⁵⁵ Freidlina, Kost, Khorlina, and Nesmeyanov, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **137**, 292 (1961).

⁵⁶ Freidlina, Khorlina, and Nesmeyanov, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, **1960**, 622.

⁵⁷ Kost, Sidorova, Freidlina, and Nesmeyanov, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **132**, 569 (1960).

trichloroethylene,³⁸ the radical addition predominates under all conditions except those in which radical initiation is excluded most rigorously. At the other extreme are compounds such as styrene and trimethylethylene which react so rapidly by the ionic mechanism that it is necessary to use high dilution techniques to obtain the products of radical addition. For the great majority of olefins which fall between these extremes, it is a fairly simple matter to effect predominantly ionic or radical addition by the use of free radical inhibitors (e.g., hydroquinone, diphenylamine, or thiophenol) or initiators (e.g., peroxides, ultraviolet light, etc.), respectively.

Aside from the necessity of avoiding ionic reaction, the choice of conditions for carrying out the free radical addition can be a rather arbitrary matter. The reaction can be run in the presence or absence of a solvent and over a temperature range from -80° or lower to $+100^{\circ}$ or higher with appropriate initiators. A wide variety of substances are effective as initiators. By far the most commonly used substances are peroxides, especially acyl peroxides such as benzoyl peroxide. In early work, the naturally occurring *endo* peroxide, ascaridole, was widely used, but it has now been largely superseded by other peroxides. The reaction can also be initiated photochemically with ultraviolet radiation of wavelength below about 2900 Å or with light of longer wavelength in combination with photosensitizers such as carbonyl compounds³⁹ or metal alkyls.⁴⁰ Ultraviolet initiation is especially convenient for low-temperature reactions, e.g., with low-boiling olefins or where stereospecificity of addition is sought. α -Haloketones initiate the reaction even in the dark,⁴¹ and finely divided metals such as iron, cobalt, and nickel are reported to be effective initiators.^{42,43} Silent electrical discharges have been used to initiate the reaction in the vapor phase,⁴⁴ but this does not suggest itself as a generally convenient preparative procedure.

The effect of solvents on the addition of hydrogen bromide to unsaturates was the subject of prolonged debate in the early studies of peroxide effects. The situation now appears to be fairly clear in view of the recognition of a competition between ionic and radical additions in most systems. The radical addition is fairly insensitive to solvent polarity, but this is not true of the ionic addition. Accordingly, the use of a non-polar solvent (e.g., pentane), which diminishes the rate of ionic addition, is favorable to the formation of the radical addition product. In fact, such reactive (ionically) olefins as styrene and trimethylethylene require high dilution in

³⁸ Kharasch, Norton, and Mayo, *J. Org. Chem.*, **3**, 48 (1938).

³⁹ Vaughan and Rust, U.S. pat. 2,398,481 (C.A., **40**, 3764 (1945)).

⁴⁰ Evans, Vaughan, and Rust, Brit. pat. 567,524, U.S. pat. 2,378,875 (C.A., **39**, 3533 (1945)).

⁴¹ Urushibara and Takebayashi, *Bull. Chem. Soc. Japan*, **11**, 692, 754 (1936) [C.A., **31**, 1757, 1758 (1937)].

non-polar media for successful radical addition. Radical addition is easily obtained in many solvents—an indication that their inhibiting properties are usually negligible. With solvents containing labile hydrogen atoms (i.e., readily transferable in radical reactions), inhibition does occur and the effect appears to increase with increasing temperature. In the presence of peroxides, no radical addition to trimethylethylene occurs above 20° in ethanol or above 0° in methanol.⁶² The ultraviolet-catalyzed addition of hydrogen bromide to allyl bromide proceeds well in heptane, carbon disulfide, acetyl bromide, or benzoyl chloride, but in acetic acid only traces of 1,3-dibromopropane are obtained.⁸ Goering and Sims²⁷ have reported that the radical additions of hydrogen bromide to 1-bromo- and 1-chlorocyclohexene can be promoted by ultraviolet light in pure pentane, in a mixture of 31 mole % diethyl ether in pentane, or in a homogeneous equimolar mixture of hydrogen chloride and pentane. However, in anhydrous ether, the reaction could not be so induced and the sole product was the 1,1-dihalide resulting from ionic addition.

The radical addition reaction appears to have a greater temperature coefficient than the ionic addition for all those hydrogen bromide-olefin combinations which have been studied. As a result, higher temperatures favor predominance of the radical reaction. For example, air does not initiate much addition of hydrogen bromide to allyl bromide at 0° , but it does at room temperature.¹² Similarly, in the addition to 1-methylcyclohexene, the ionic addition product is formed exclusively at -80° , but at 0° it constitutes only 64% and at 65° only 22% of the total adduct.²⁶ Nevertheless, it is often possible to effect radical additions to the complete exclusion of ionic reaction even at temperatures as low as -80° . This can be of considerable significance in stereospecific additions wherein the thermodynamically less stable isomer is sometimes formed.

RADICAL ADDITIONS TO CARBON-CARBON UNSATURATES TO FORM SULFUR-CARBON BONDS

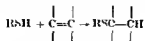
Several species of sulfur compounds, e.g., thiols, hydrogen sulfide, bisulfite ion, sulfonyl halides, sulfur chloride pentafluoride, sulfonyl and sulfonyl halides, add by radical mechanisms to olefinic and acetylenic compounds to form carbon-sulfur bonds. Each of these classes constitutes a relatively large subject and will be considered separately. The radical copolymerization of sulfur dioxide with olefins* also involves the formation of carbon-sulfur bonds, but, since it is of rather specialized interest, it has not been included in this chapter.

⁶² Michael and Weiner, *J. Org. Chem.*, **4**, 531 (1939).

* Olefin-sulfur dioxide copolymerizations have been reviewed by Walling in ref. 45, p. 223.

Addition of Thiols to Olefins and Acetylenes

Thiols add to olefins and acetylenes via a free radical chain mechanism to form sulfides. The reaction is characteristic of thiols generally, e.g., hydrogen sulfide (p. 191), alkanethiols, aromatic and heterocyclic thiols,



thiocarboxylic acids, and thiophosphoric acids. The usual free radical initiators, such as oxygen, peroxides, azonitriles, and ultraviolet radiation, are effective in initiating the reaction.

Apparently the first recorded example of the reaction was the anti-Markownikoff addition of thiophenol to styrene reported by Posner in 1905.⁶³ Ashworth and Burkhardt, repeating Posner's experiments in

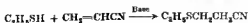


1928, noted that exposure to sunlight produced a significant acceleration in the rate of addition and that piperidine retarded it.⁶⁴ Subsequently Burkhardt postulated the phenylthiyl radical ($\text{C}_6\text{H}_5\text{S}\cdot$) as an intermediate in the reaction.⁶⁵ The catalytic influence of peroxides was reported in 1938 by Kharasch, Read, and Mayo⁶⁶ and by Jones and Reid.⁶⁷ The currently accepted radical chain mechanism was formulated by Kharasch, Read, and Mayo in that year.⁶⁶

Addition of thiols to unsaturates can also occur by ionic mechanisms. Examples are acid-⁶⁸ or sulfur-⁶⁷catalyzed addition to olefins and acetylenes and base-catalyzed addition to α,β -unsaturated carbonyl com-



pounds and nitriles.⁶⁹ These ionic additions generally give products



resulting from normal (Markownikoff) addition, whereas radical additions are characteristically abnormal. Jones and Reid⁶⁷ were the first to demonstrate that either normal or abnormal 1:1 adducts can be obtained from addition of a thiol to an olefin, depending upon the catalyst used

⁶³ Posner, *Ber.*, **38**, 846 (1905).

⁶⁴ Ashworth and Burkhardt, *J. Chem. Soc.*, **1928**, 1791.

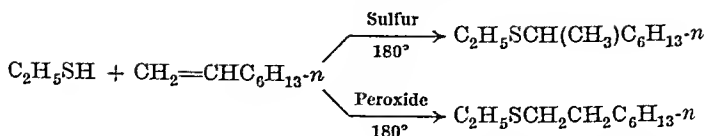
⁶⁵ Burkhardt, *Trans. Faraday Soc.*, **30**, 18 (1934).

⁶⁶ Kharasch, Read, and Mayo, *Chem. & Ind. (London)*, **57**, 752 (1938).

⁶⁷ Jones and Reid, *J. Am. Chem. Soc.*, **60**, 2452 (1938).

⁶⁸ Ipatieff, Pines, and Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938).

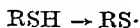
⁶⁹ Kharasch and Fuchs, *J. Org. Chem.*, **13**, 97 (1946).



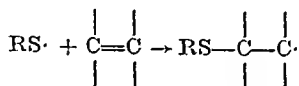
Radical and ionic additions to α,β -unsaturated carbonyl compounds and nitriles lead to the same product. Reviews of the additions of thiols to olefins have been made by Mayo and Walling,⁸ Walling (ref. 45, pp. 313 ff.), and Knunyants and Fokin.⁷⁰

Mechanism. Studies of the mechanism of radical thiol additions have dealt largely with additions to olefins. Acetylene additions have apparently not been studied in this respect. The reaction is generally considered to proceed via a multistep chain mechanism.^{66,71} The chain

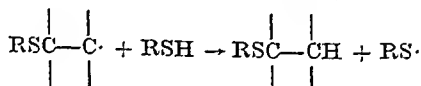
Initiation:



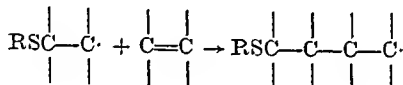
Addition:



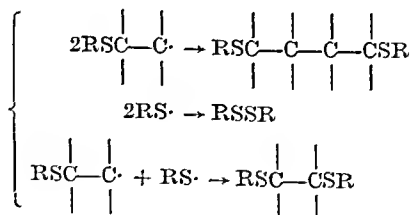
Chain transfer:



Propagation:



Termination:



nature of the reaction is indicated by the acceleration produced by ultra-violet radiation and by the observation that, in reactions initiated by free radical initiators, only minute amounts of these materials are required. Kinetic chain lengths of 10^4 have been reported.⁷¹ Each step in the mechanism shown will be discussed in some detail in the following paragraphs.

Initiation. Generation of a thiyl radical from a thiol can be accomplished by means of the decomposition of a peroxide, an azonitrile, or other radical-generating species in the reaction mixture, by irradiation

⁷⁰ Knunyants and Fokin, *Usp. Khim.*, **19**, 545 (1950).

⁷¹ Back, Trick, McDonald, and Sivertz, *Can. J. Chem.*, **32**, 1078 (1954).

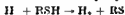
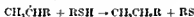
of the thiol with α -rays,⁶⁷ γ -rays,⁷²⁻⁷³ or β -rays,⁷⁴ or by direct photolysis of the thiol with ultraviolet radiation. The mechanism of initiation with radical-producing agents consists of abstraction of hydrogen from a thiol molecule by a radical produced in the reaction mixture, thus a thiyl



radical is generated. When ultraviolet radiation capable of thiol photolysis is employed, both a thiyl radical and a hydrogen atom are produced.⁷⁵ Likely fates for the hydrogen atom are (a) addition to the olefin ultimately



producing a thiyl radical and a molecule of alkane, and (b) attack on the thiol to produce molecular hydrogen and a thiyl radical.



Thus, in ultraviolet initiation, both radical species produced can start kinetic chains. Since the reactions producing the 1:1 adduct are generally of great chain length, the yield of molecular hydrogen and alkane will be small compared to the yield of the olefin-thiol addition product. However, in the photoinitiated addition of butanethiol to vinyl acetate, both hydrogen and ethyl acetate have been found.⁷⁶

Addition and Chain Transfer In a typical thiol addition, both the addition and the chain transfer are quite exothermic, and thus, once the thiyl radical is generated, a rapid chain reaction can ensue (ref. 45, pp. 313 ff)



There is ample evidence that in some cases the addition step is reversible.^{25,77-80} On the basis of determination of negative over-all activation energies for gas phase photoinitiated addition of methanethiol to isobutylene, propylene, and ethylene, Sivertz and co-workers concluded

⁷² Fontijn and Spinks, *Can. J. Chem.*, **35**, 1384, (1957).

⁷³ Fontijn and Spinks, *Can. J. Chem.*, **35**, 1397 (1957).

⁷⁴ Chingman, *J. Phys. Chem.*, **84**, 1355 (1960).

⁷⁵ Inaba and Darwent, *J. Phys. Chem.*, **64**, 1431 (1960).

⁷⁶ Yamagishi, Araki, Suzuki, and Hoshino, *Bull. Chem. Soc. Japan*, **33**, 528 (1960).

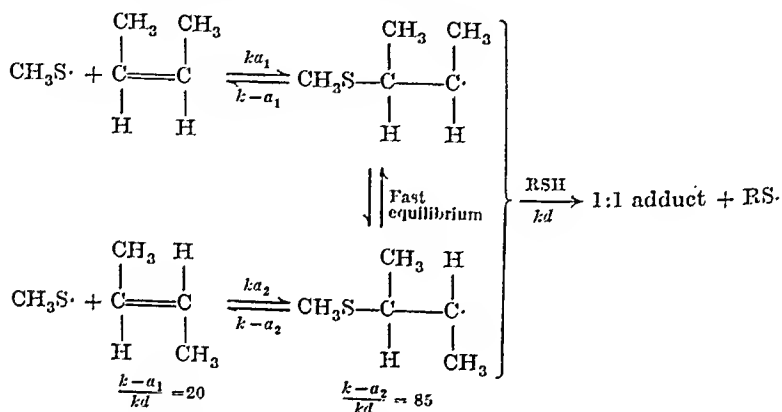
⁷⁷ Sivertz, Andrews, Elsdon, and Graham, *J. Polymer. Sci.*, **19**, 587 (1956).

⁷⁸ Fallon and Sivertz, *Can. J. Chem.*, **35**, 723 (1957).

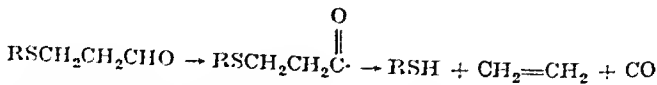
⁷⁹ Sivertz, *J. Phys. Chem.*, **63**, 34 (1959).

⁸⁰ Walling and Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

that the addition step in these reactions is reversible.⁷⁷ Experimentally, the isomerization of pure *cis*- or *trans*-olefins by small amounts of thiol has been given as evidence for reversibility of the addition step. For example, either *cis*- or *trans*-2-butene is equilibrated by small amounts of methanethiol,⁸⁰ indicating that the thiyl radical adds to the olefin to give an intermediate radical which equilibrates and then largely dissociates to the thiyl radical and a mixture of the *cis*- and *trans*-olefin. At 60°, the reverse reactions are 20 and 85 times as fast as the chain transfer step for the *cis* and *trans* isomers, respectively.⁸⁰



Similarly, *cis*- or *trans*-2-butene is isomerized by small amounts of thioacetic acid upon ultraviolet irradiation at room temperature, but at -78° no isomerization occurs.²⁵ With terminal olefins, and with olefins from which resonance-stabilized intermediate radicals are formed by addition of a thiyl radical (e.g., β -methylstyrene and methyl acrylate), the addition step is considerably less reversible.⁸⁰ The formation of thiol and olefin in the decarbonylation of β -alkylmercaptoaldehydes affords additional evidence of the reversibility of the addition step.⁸¹

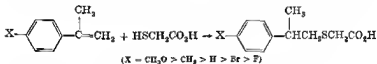


A vast amount of information concerning the relative reactivities of thiols in the chain transfer step has been obtained from the determination of thiol transfer constants in vinyl polymerizations (ref. 45, p. 319). From such studies it has been found that thiols with electron-withdrawing groups (e.g., CO_2H , C_6H_5) are enhanced in reactivity, whereas those with

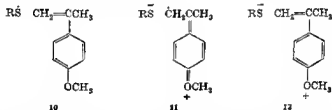
⁸¹ Foster, Larchar, Lipacomb, and McKusick, *J. Am. Chem. Soc.*, **78**, 5696 (1956).

electron-donating groups (e g, *t*-butyl and *t*-octyl) are less reactive than primary alkanethiols.

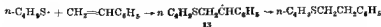
Kinetic studies^{71-74 78-80 82} have afforded considerable insight into the effect of structure on reactivity, particularly with respect to the addition and transfer steps. It has been claimed that thyl radicals are electrophilic in nature, since in a series of competitive experiments involving the addition of mercaptoacetic acid to substituted α -methylstyrenes it was found that electron-donating groups in the *p*-position increase the rate of reaction.⁸³



Polar structures 11 and 12 contributing to the transition state have been proposed to account for this effect *



The effects of structure on the rates of both the addition step and the chain transfer step leading to the 1:1 adduct have been studied by Sivertz^{71,78,82} and by Walling⁸⁰. Generally, the transfer step is the slower, rate-determining step, being first order in the thiol †. For example, the intermediate radical in the *n*-butanethiol-styrene reaction is a resonance-stabilized radical 13; consequently, the addition step leading to its formation is relatively fast and the transfer step is relatively slow (Table II)⁷⁸



⁸² Onyszchuk and Sivertz, *Can. J. Chem.*, **33**, 1634 (1955)

⁸⁰ Walling, Seymour, and Wolfstam, *J. Am. Chem. Soc.*, **70**, 2559 (1948)

* Such relative rates can also be correlated with the relative stabilities of the intermediate benzyl radicals, i.e., the more stable the intermediate benzyl radical, the faster is the rate of its formation. An experiment with *p*-nitro- or *p*-cyano α -methylstyrene might help to establish the more meaningful correlation.

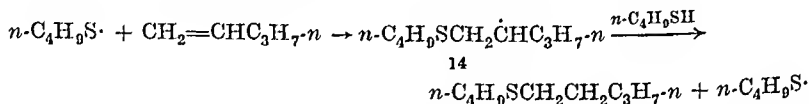
† If the addition step were the slow step, the rate of the over all reaction would depend on the olefin concentration.

TABLE II^{78,79}

ADDITION, TRANSFER, AND TERMINATION RATES
(LITERS/MOLES SEC.) AT 25°

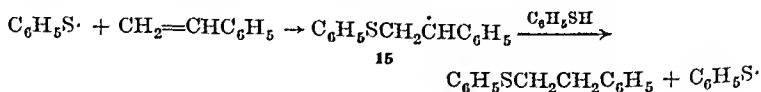
	<i>k</i> (Addition)	<i>k</i> (Chain Transfer)	<i>k</i> (Termination)
<i>n</i> -Butanethiol-styrene	1.2×10^9	1.24×10^3	5×10^8
<i>n</i> -Butanethiol-1-pentene	7×10^6	1.4×10^6	6×10^{11}
Thiophenol-styrene	—	3×10^3	2×10^7
<i>n</i> -Butanethiol-isoprene	—	93	1.4×10^8

In the addition of *n*-butanethiol to 1-pentene, the addition step is slow



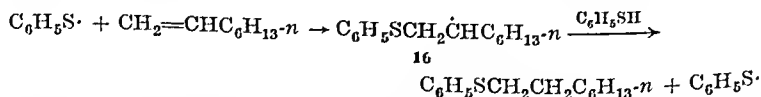
relative to the *n*-butanethiol-styrene reaction since no resonance stabilization is possible in the intermediate radical 14. For the same reason, the transfer step is fast relative to the *n*-butanethiol-styrene reaction (Table II). The rates of the two steps in the *n*-butanethiol-pentene reaction are close enough that the over-all rate of reaction shows some dependence on the olefin concentration, although it is still largely first-order in the thiol. A consequence of the difference between the rates of the addition steps in the *n*-butanethiol-styrene and *n*-butanethiol-pentene additions is that, even though the over-all rate of the *n*-butanethiol-pentene reaction is 20 times that of the *n*-butanethiol-styrene reaction, in a competitive experiment styrene reacts preferentially.

In the addition of thiophenol to styrene the transfer step is again rate-



controlling (first-order in thiol) owing to the large resonance stabilization possible in the intermediate radical 15.⁷⁸

In contrast to the preceding systems, the over-all rate of the thiophenol-1-octene reaction is first-order in both thiol and olefin.⁷⁸ Although no



values for the individual rates have been given, it seems that here the addition step is slower than that in the previously discussed cases since it

involves the addition of a resonance-stabilized phenylthiyl radical to form an intermediate radical 16 which is not resonance-stabilized. The transfer step should be relatively fast compared to the previously discussed systems since it results in the formation of the phenylthiyl radical. The over-all rate of the thiophenol-1-octene reaction is less than that of the thiophenol-styrene reaction, presumably because of the slow addition step in the octene reaction.⁷⁸

From the discussion above and from a series of competitive experiments of dodecanethiol at 60° with several olefins (Table III),⁸² the following

TABLE III
RELATIVE REACTIVITIES OF OLEFINS TOWARD
DODECANETHIOL AT 60°⁸²

Olefin	Relative Reactivity	Olefin	Relative Reactivity
Styrene	17	Allylbenzene	1.0
β -Methylstyrene	5.5	Vinyl acetate	0.8
Vinyl <i>n</i> -butyl ether	3.9	Allyl chloride	0.7
Methyl methacrylate	2.4	Cyclopentene	0.6
Methyl acrylate	2.0	Allyl acetate	0.6
Allyl alcohol	1.5	Allyl cyanide	0.4
2-Methyl-1-butene	1.2	Cyclohexene	0.3
1-Octene	1.0	<i>cis</i> -Dichloroethylene	<0.2

conclusions concerning the effect of olefin structure on the rate of the addition step can be drawn: (a) reactivity is increased if the intermediate radical is resonance-stabilized and, conversely, it is decreased if the thiyl radical is resonance-stabilized; (b) electron-donating groups in the olefin increase the rate, while electron-withdrawing groups decrease the rate; (c) terminal double bonds are more reactive than internal ones; (d) cyclopentene is more reactive than cyclohexene.

Propagation. The importance of propagation leading to telomers depends on the nature of the olefin and on the transfer activity of the thiol. Generally, if the olefin undergoes radical polymerization easily, telomer formation will occur. It can be minimized by use of a large excess of the thiol. In kinetic terms,* propagation becomes important if the rate of the

* Considerable attention from the kinetic point of view has been given to the relationship between chain transfer and propagation in radical polymerization of olefins in the presence of thiols. A discussion of this work is considered to be outside the scope of this chapter. For pertinent references see Walling⁴⁴ (also ref. 45, Chapters 4 and 7), Hutt and Bartlett,⁴⁵ Gregg, Alderman, and Mayo.⁴⁶

⁴⁴ Walling, *J. Am. Chem. Soc.*, **70**, 2551 (1948).

⁴⁵ Hutt and Bartlett, *J. Am. Chem. Soc.*, **81**, 1143 (1959).

⁴⁶ Gregg, Alderman, and Mayo, *J. Am. Chem. Soc.*, **70**, 3746 (1948).

reaction of the intermediate radical with a molecule of olefin is comparable to the rate of reaction with the thiol. The ratio of these rates has been defined as the transfer constant, C , and is specific for each thiol-olefin combination. Because thiol transfer constants are generally high, in

$$C = \frac{\text{rate of transfer}}{\text{rate of propagation}}$$

reaction mixtures of equimolar amounts of reactants the 1:1 adduct will predominate. Transfer constants for *n*-butanethiol and typical polymerizable olefins are shown in Table IV.

TABLE IV

TRANSFER CONSTANTS OF *n*-BUTANETHIOL AT 60°⁸⁴

Vinyl acetate	48
Styrene	22
Methyl acrylate	1.69
Methyl methacrylate	0.67

An example illustrating the importance of the nature of the thiol on the rate of transfer vs. propagation is seen in the reactions of trifluoromethanethiol and methanethiol with chlorotrifluoroethylene carried out under comparable conditions (Table V).⁶ Although no values have been derived, the transfer constant of trifluoromethanethiol is obviously much lower than that of methanethiol.

TABLE V

YIELDS (%) OF ADDUCTS IN ULTRAVIOLET-INITIATED ADDITIONS OF CH₃SH AND CF₃SH TO CFCI=CF₂

	1:1 Adduct (%)	2:1 Adduct (%)	3:1 Adduct (%)
CH ₃ SH	84	5	—
CF ₃ SH	62	20	3

Other olefins that have been reported to give telomers in thiol additions are tetrafluoroethylene (CF₃SH⁶ and C₂H₅SH⁸⁷), trifluoroethylene (CF₃SH),⁶ acrylic esters (C₂H₅SH,⁶⁹ *n*-C₃H₇SH,⁶⁹ *n*-C₁₂H₂₅SH⁸⁹), styrene (*n*-C₁₂H₂₅SH),⁹⁰ and methyl methacrylate (C₆H₅SH, *m*- and *p*-CH₃C₆H₄SH).⁹¹

⁸⁷ Hanford, U.S. pat. 2,443,003 [C.A., 42, 6841 (1948)].

⁸⁹ Ipatieff and Friedman, *J. Am. Chem. Soc.*, 61, 71 (1939).

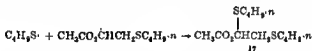
⁹⁰ Hachiama and Sumitomo, *Technol. Repts. Osaka Univ.*, 7, 463 (1957) [C.A., 53, 3044 (1959)].

⁹¹ Kharasch, Nudenberg, and Meltzer, *J. Org. Chem.*, 18, 1233 (1953).

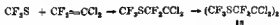
⁹² Jacobson, U.S. pat. 2,199,799 [C.A., 34, 5968 (1940)].

Termination. The three reactions shown on p. 166 have been proposed as the chain termination processes for radical thiol additions,⁷¹ but relatively little study has been devoted to them. In Table 11 are tabulated the over-all termination rates, determined by rotating sector techniques, of several olefin-thiol addition reactions.⁷² In comparison with the rates of the corresponding addition and chain transfer steps, the termination steps are very fast, probably requiring activation energies of only a few hundred calories.⁷¹ Since the kinetic chain lengths of thiol addition reactions are usually high, the yields of the chain termination products will be very low indeed, and generally these products have not been detected.

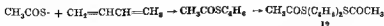
However, in some additions the yields of chain termination products may become appreciable. Yields up to 10% of diaryl disulfides, ArSSAr, have been found in the products from the ultraviolet-initiated additions of thiophenols to 1-chlorocyclohexene and 1-chlorocyclopentene.⁷² In the photoinitiated addition of *n*-butanethiol to vinyl acetate employing a large excess of the thiol (20:1 mole ratio), isolable amounts of the cross-termination product 17 were obtained in addition to the usual 1:1 adduct.⁷³



In the addition of trifluoromethanethiol to 1,1-difluorodichloroethylene, the intermediate radical formed is apparently quite stable, not readily undergoing transfer with the thiol or adding to the olefin. It dimerizes to a large degree giving the additive dimer 18 as a major product.⁹³



Another example of the production of the additive dimer in major proportions is seen in the reaction of thiolacetic acid with butadiene under conditions where the thiol and a stoichiometric amount of initiator (hydroxyl radicals) are added to the reaction mixture simultaneously. Under these conditions there is virtually no thiol available for chain



transfer and the major product is the additive dimer 19.⁷⁴

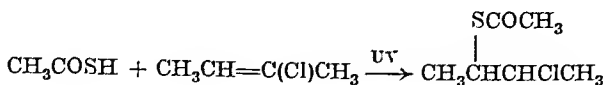
Stereochemistry. The radical addition of thiols to non-cyclic olefins is not stereospecific. Apparently there is a rapid equilibration of the

⁷¹ Goering, Relyea, and Howe, *J. Am. Chem. Soc.*, **79**, 2502 (1957).

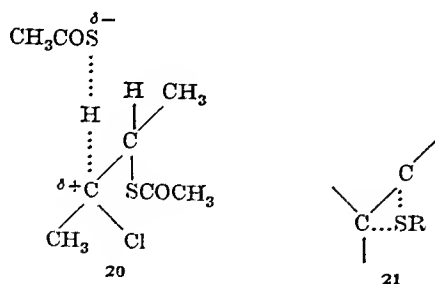
⁷² Harris, J. F., Jr. Unpublished experiments.

⁷⁴ Jenner and Lindsey, *J. Am. Chem. Soc.*, **83**, 1911 (1961).

intermediate radical before the chain transfer step can occur. For example, addition of methanethiol-*d* to *cis*- and *trans*-2-butene gives the same mixture of *threo*- and *erythro*-3-deutero-2-methylthiobutanes.⁹⁵ Similarly, the addition of thiolacetic acid to both *cis*- and *trans*-2-chloro-2-butene yields the same mixture of 3-chloro-2-acetylthiobutanes under conditions where no isomerization of the olefin occurs, thus indicating a common intermediate from both olefins.²⁵ A rationalization for the



predominance of the *threo* isomer in the latter case has been offered which assumes the development of a dipole in the transition state of the transfer step and orientation of the largest negative dipole on the saturated carbon away (*trans*) from the developing dipole. This, considered with minimum steric requirements, predicts **20** (the *threo* precursor) as the transition state of lowest energy. The lack of stereospecificity in these

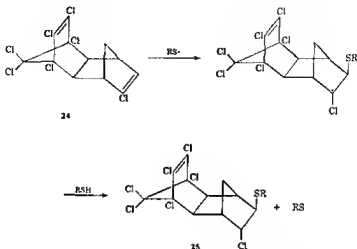


additions indicates that no bridged-type structure such as **21**, similar to that formulated in the ionic addition of sulphenyl chlorides to olefins,⁹⁶ is involved in the radical addition of thiols.

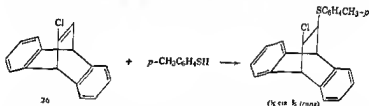
Stereospecific *trans* addition of the elements of methanethiol-*d* has been achieved at -78° in mixtures of an olefin, deuterium bromide, and methanethiol-*d*.⁹⁵ Thus *cis*- and *trans*-2-butene yield *threo*- and *erythro*-3-deutero-2-methylthiobutane, respectively. In these cases, a rapid chain transfer with deuterium bromide apparently takes place before equilibration of the intermediate radical can occur.

⁹⁵ Skell and Allen, *J. Am. Chem. Soc.*, **82**, 1511 (1960).

⁹⁶ Kharasch and Bueh, *J. Am. Chem. Soc.*, **71**, 2724 (1949).



to an appreciable extent, if at all, since they should lead to exclusive *trans* addition. Since rearranged products were not observed, there is no



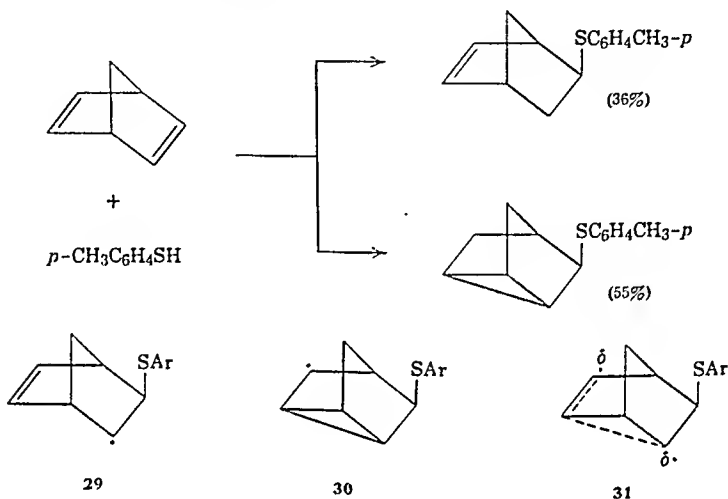
support for non-classical mesomeric type intermediate radicals such as 28 analogous to intermediates involved in ionic reactions of these bicyclic systems.



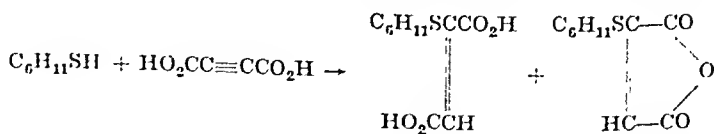
The addition of *p*-thioresol to 2,5-norbornadiene gives two products, both having the *exo* configuration.³⁰³ On the basis of kinetic studies it has been determined that the products arise from two separate intermediates,

³⁰³ Cristol, Brundell, and Reader, *J. Am. Chem. Soc.*, **80**, 635 (1958)

29 and 30, rather than from a single mesomeric intermediate, 31. Thus, after the thiyl radical adds to one of the double bonds to form the radical intermediate 29, rearrangement to the substituted nortricyclic radical 30 occurs at a finite rate, followed by chain transfer by both radicals. Here again there is no need to postulate (and no evidence to support) the non-classical radical intermediate 31.



No detailed study of the stereochemistry of thiol-acetylene additions has been made. Several products, however, have been reported which obviously arise from predominant *trans* addition. For example, addition of cyclohexanethiol to acetylenedicarboxylic acid yielded mainly the substituted fumaric acid accompanied by a small amount of the corresponding maleic anhydride.¹⁰⁴ Similarly, addition of benzyl mercaptan to propiolic

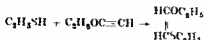


acid yielded the *cis* isomer of β -benzylmercaptoacrylic acid.¹⁰⁵ The addition of ethanethiol to ethoxyethyne at -10° afforded largely the *cis* isomer of 1-ethoxy-2-(ethylthio)ethylene, which partly isomerized to the *trans* isomer on distillation or long standing at room temperature.¹⁰⁶

¹⁰⁴ Weibull, *Arkiv Kemi*, **3**, 225 (1951) [*C.A.*, **46**, 3965 (1952)].

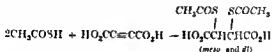
¹⁰⁵ Owen and Sultanbawa, *J. Chem. Soc.*, **1949**, 3109.

¹⁰⁶ Alkema and Arens, *Rec. Trav. Chim.*, **79**, 1257 (1960).



Similarly, the addition of ethanethiol to ethyl ethynyl sulfide gave the *cis* adduct¹⁰⁷

The addition of a second thiol molecule is of course non-stereospecific (as in thiol-olefin additions), and both the *meso* and *dl* forms were obtained from the addition of two moles of thiolacetic acid to acetylenedicarboxylic acid¹⁰⁸



Scope and Limitations. *Olefins.* Radical addition of thiols to olefins and acetylenes, a reaction of extremely wide scope, has been used to prepare an enormous variety of sulfides. All types of thiol compounds, including hydrogen sulfide (p 191), thiophosphoric acids, mono- and di-basic thiocarboxylic acids, heterocyclic thiols, aromatic mono- and di-thiols, and alkane mono- and di-thiols enter into the reaction readily. Secondary thiols, tertiary thiols (e.g., *t*-butyl mercaptan^{109,110}), alicyclic thiols (e.g., cyclohexanethiol), and alkanethiols containing the neighboring substituents OH, F, Cl, CO₂H, and COR all work well.

Relatively few studies have been made of comparative reactivities of thiols. In studies of additions to styrene, the following order of over-all thiol reactivity has been reported:¹¹¹ ArylSH > HO₂CCH₂SH > RCH₂SH > RR'CHSH > RR'R'CSH. Cunneen^{108,112} observed the following order of reactivity in the addition of a series of thiols to cyclohexene, dihydromyrcene, squalene, and natural rubber: Cl₂CCOSH > Cl₂CHCOSH > ClCH₂COSH > CH₃COSH > HO₂CCH₂SH > C₆H₅SH > (CH₃)₂CHCH₂CH₂SH. This sequence roughly parallels the order of acidity of the thiols. Benzyl mercaptan is reported to be less reactive than thiolacetic acid¹¹³

Most olefins, linear and cyclic, undergo radical thiol addition readily. Terminally unsaturated hydrocarbons are more reactive than their internally unsaturated or cyclic counterparts, and the RS group invariably

¹⁰⁷ Shostakovskii, Prilezhaeva, Tsymlal, and Stolyarova, *J. Gen. Chem. USSR (Engl. Transl.)*, **30**, 3116 (1960).

¹⁰⁸ Cunneen, *J. Chem. Soc.*, **1947**, 36.

¹⁰⁹ Vinton, U.S. pat. 2,607,775 (C.A., **47**, 6989 (1953)).

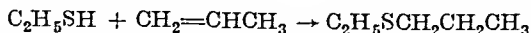
¹¹⁰ Yamaguchi and Nakazawa, *Nippon Kagaku Zasshi*, **75**, 1086 (1954) [C.A., **51**, 14596 (1957)].

¹¹¹ Kharsach, Nudenberg, and Mantell, *J. Org. Chem.*, **16**, 524 (1951).

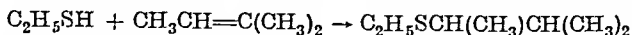
¹¹² Cunneen, *J. Chem. Soc.*, **1947**, 134.

¹¹³ Brown, Jones, and Pinder, *J. Chem. Soc.*, **1951**, 3315.

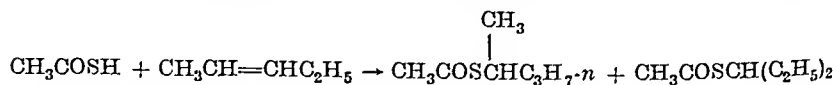
becomes attached to the terminal carbon atom, as in the addition of ethanethiol to propylene.⁸⁸ Olefins with considerable branching about



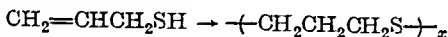
the double bond (e.g., 3-methyl-2-butene) may also be employed, and the product is that predicted from the more stable intermediate radical.⁸⁸



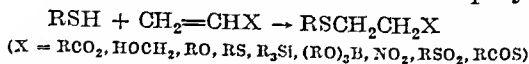
From internal olefins with similar hydrocarbon substituents, both 1:1 adducts are obtained. Thus nearly equal amounts of the two possible thiolacetates are obtained in the addition of thioacetic acid to 2-pentene.¹¹⁴



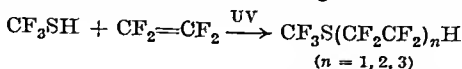
Unsaturated thiols (e.g., allyl mercaptan,^{115,116} crotyl mercaptan,¹¹⁵ 3-mercaptopentene,¹¹⁵ 4-mercaptopentene,¹¹⁵ 5-mercaptopentene,¹¹⁵ cinnamyl mercaptan,¹¹⁷ 4-mercaptopentylcyclohexene,¹¹⁸ and 3-methyl-2-butene-1-thiol¹¹⁵) have been reported to undergo self-addition, usually spontaneously. Neither the reactions nor the products have received extensive investigation.



Ethylenes with a variety of substituents containing hetero atoms have been used. The product is that shown in the accompanying equation.



Addition of trifluoromethanethiol to tetrafluoroethylene yields a series of telomers with the 1:1 adduct predominating.⁶ The addition of thiols to



other highly fluorinated but unsymmetrical terminal olefins generally leads to a single 1:1 adduct whose orientation can be predicted from the more stable intermediate radical.^{6,119} Addition of methanethiol, trifluoromethanethiol, and 2,2,2-trifluoroethanethiol to hexafluoropropene, however, yields both 1:1 adducts, the relative amounts depending on the

¹¹⁴ Hewett, W. A., Doctoral Dissertation, Northwestern University, 1955; *Dissertation Abstr.*, 16, 24 (1956).

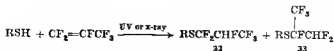
¹¹⁵ vonBraun and Plate, *Ber.*, 67, 281 (1934).

¹¹⁶ Ayers and Scott, U.S. pat. 2,738,341 [*C.A.*, 50, 11720 (1956)].

¹¹⁷ vonBraun and Murjahn, *Ber.*, 59, 1202 (1926).

¹¹⁸ Marvel and Olson, *J. Polymer Sci.*, 26, 23 (1957).

¹¹⁹ W. L. Thompson, Doctoral Dissertation, Cornell University, 1955; *Dissertation Abstr.*, 16, 243 (1956).



nature of the thiol (Table VI).⁸ Consideration of the stabilities of intermediate radicals leads to the prediction of 32 as the favored product, but in fact 33 is the predominant adduct from trifluoromethanethiol. A correlation between the relative electrophilicities ($\text{CF}_3\text{S}\cdot > \text{CF}_3\text{CH}_2\text{S}\cdot > \text{CH}_3\text{S}\cdot$) of the adding radical and the relative abundance of adduct 33,

TABLE VI

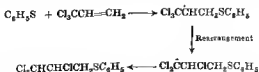
1.1 ADDUCT COMPOSITION FROM ADDITION OF THIOLS (RSH) TO HEXAFLUOROPROPENE

R	1.1 Adduct Composition	
	32 (%)	33 (%)
CF_3	45	55
CF_3CH_3	70	30
CH_3	92	8

whose formation requires attachment of the thiyl radical to the negatively polarized carbon of hexafluoropropene (34), can be made.⁸ One attempt to add a thiol to an internal perfluoroolefin (perfluoro-2 butene) failed,⁸



Other highly halogenated olefins have scarcely been studied, although additions occur readily to vinyl chloride¹²⁰ and to other olefins with one chlorine atom on the double bond.⁹² The ultraviolet-initiated addition of thiophenol to 3,3,3 trichloropropene proceeds with a rearrangement that apparently involves migration of a chlorine atom in the intermediate radical.¹²¹

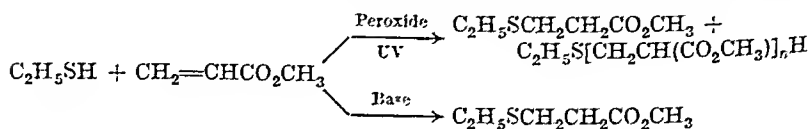


A similar rearrangement was observed in the reaction of benzyl mercaptan with this olefin.

¹²⁰ Hoshino and Yamagishi, *Jap. pat.* 6,480 [*C.A.*, **49**, 2689 (1955)].

¹²¹ Nesmeyanov, Fridlana, Petrova, and Terent'eva, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **127**, 591 (1959).

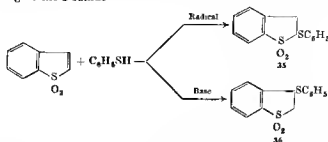
Radical addition of thiols to α,β -unsaturated carbonyl compounds and nitriles gives the 1:1 adduct with the RS group on the β -carbon atom. The same adduct is obtained when the reaction proceeds by a polar mechanism. The two pathways have been studied separately with ethanethiol and methyl acrylate, which, when mixed in the absence of a catalyst, do not react.⁶⁹ If a small amount of ascaridole is added and the mixture irradiated, an exothermic reaction ensues yielding methyl 2-ethylthiopropionate and telomers containing two, three, and more molecules of methyl acrylate. If, instead of peroxide, a small amount of trimethylbenzylammonium hydroxide ("Triton B") is added, a rapid reaction takes place which produces the 1:1 adduct in 95% yield. Since



no reaction occurs unless a catalyst is added, it is possible to direct the reactants into either a radical or ionic reaction. However, many analogous reactions occur without the addition of a catalyst, and in most of them it has not been determined whether the reaction follows an ionic or a free radical pathway.¹²²⁻¹⁴⁹

Radical addition of thiophenol to benzothiophene-1-dioxide produces the 2-substituted sulfide 35, presumably because of the resonance stabilization

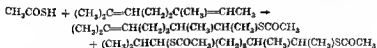
possible in the intermediate benzyl-type radical ¹⁴¹ Under base catalysis, the 3-substituted sulfide **36** is obtained. Aliphatic thiols under all conditions give the 3-sulfide



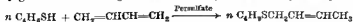
Additions of thiol acids, mainly thiolacetic acid, to a series of unsaturated ketosteroids (e g, $\Delta^{1,4}$ -3-oxo-, $\Delta^{1,6}$ -3-oxo-, and $\Delta^{1,4,6}$ -3-oxo-steroids) have been reported. In view of the rather specialized nature of the compounds involved, these additions, which are all tabulated in two articles,^{142,143} are not included in the table of thiol acid additions.

Several monoolcfinic compounds have been reported to be inert to radical thiol additions. Thiolacetic acid failed to add to stilbene in the presence of peroxide¹⁴⁴ Similarly, thiolacetic acid failed to react with cinnamyl alcohol,¹⁴⁴ but the ascaridole-catalyzed addition of benzyl mercaptan proceeded in 47% yield.¹¹³ Methyl cinnamate was reported not to react with *p*-thiocresol or benzyl mercaptan,¹²³ yet cinnamic acid formed an adduct with benzyl mercaptan in the presence of peroxide.¹¹³

Non-conjugated dienes (e g, dihydromyrcene) furnish mono- and di-adducts,¹¹² the relative amounts depending on the ratio of the reactants.



Conjugated dienes undergo 1,4 addition only^{145,146} The geometry of the



diene apparently makes no difference in the choice of 1,4 over 1,2 addition, since both 1,2-dimethylenecyclohexane and 3-methylenecyclohexene gave only 1,4 adducts¹⁴⁷

¹⁴¹ Bordwell, Chapman, and McKellop, *J. Am. Chem. Soc.*, **76**, 3637 (1954).

¹⁴² Dodson and Twent, *J. Am. Chem. Soc.*, **81**, 1224 (1959).

¹⁴³ Twent and Dodson, *J. Org. Chem.*, **24**, 277 (1959).

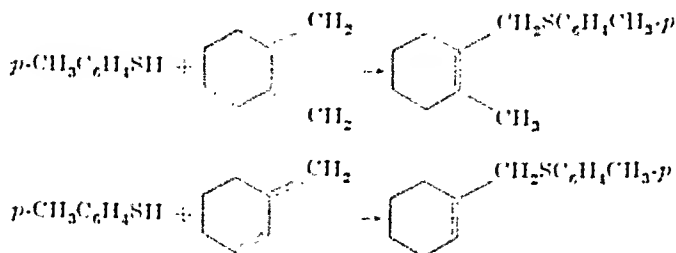
¹⁴⁴ Brown, Jones, and Pinder, *J. Chem. Soc.*, **1951**, 2123.

¹⁴⁵ Longfield, Jones, and Siverts, *Can. J. Res.*, **26B**, 373 (1950).

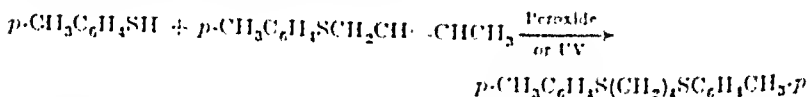
¹⁴⁶ Marvel and Cripps, *J. Polymer Sci.*, **8**, 313 (1953).

¹⁴⁷ Cristol and Nagpal, *J. Org. Chem.*, **26**, 365 (1961).

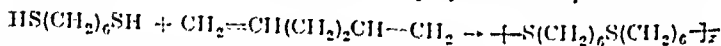
If the reaction is forced so that a second mole of thiol adds, a rearrangement occurs and the product is a 1,4-bis-sulfide.^{118,119} The nature of



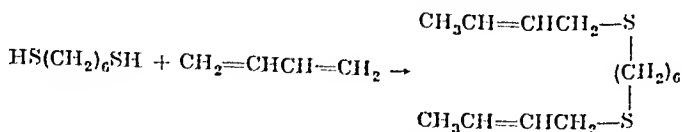
this rearrangement is not understood.



Radical additions of dithiols to diolefins lead to polymeric materials.^{118,150,151} The dithiols which have been used include aliphatic dithiols,¹⁴⁸ aromatic dithiols,¹⁵² and dibasic aliphatic and aromatic thiol acids.¹⁵³ The diolefins employed have generally been non-conjugated; e.g., biallyl. Most widely studied is the biallyl-hexamethylenedithiol system which leads to the formation of polyhexamethylene sulfide.^{151,155}



Conjugated olefins are generally unsatisfactory since the initial 1,4 addition gives allyl type sulfides which do not undergo further addition readily. Thus the reaction of hexamethylenedithiol with 1,3-butadiene leads to the formation of 1,6-bis-(crotylmercapto)hexane, which is inert to further reaction.¹⁴⁶ Similarly, allyl sulfide does not form polymers with hexamethylenedithiol,^{146,156} but allyl ether does.¹⁴⁶



¹⁴⁸ Marvel and Chambers, *J. Am. Chem. Soc.*, **70**, 993 (1948).

¹⁴⁹ J. A. Reeder, Doctoral Dissertation, *Dissertation Abstr.*, **20**, 3960 (1960).

¹⁵⁰ Marvel, *Record Chem. Progr. (Kresge-Hooker Sci. Libr.)*, **12**, 185 (1951).

¹⁵¹ Marvel, Hinman, and Inskip, *J. Am. Chem. Soc.*, **75**, 1997 (1953).

¹⁵² Marvel and Caesar, *J. Am. Chem. Soc.*, **73**, 1097 (1951).

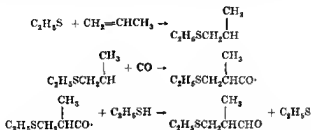
¹⁵³ Marvel and Kotch, *J. Am. Chem. Soc.*, **73**, 1100 (1951).

¹⁵⁴ Marvel and Markhart, *J. Am. Chem. Soc.*, **73**, 1084 (1951).

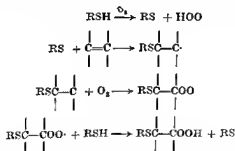
¹⁵⁵ Marvel and Aldrich, *J. Am. Chem. Soc.*, **72**, 1978 (1950).

¹⁵⁶ Marvel and Markhart, *J. Polymer Sci.*, **6**, 711 (1951).

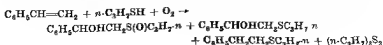
When thiols, olefins, and carbon monoxide are heated at 3000 atm. pressure with a peroxide catalyst, aldehydes are produced in addition to the olefin-thiol adduct.⁸¹ For example, propylene, ethanethiol, carbon monoxide, and di-*t*-butyl peroxide at 130° produce 3-ethylthio-2-methylpropanal (16%) and ethyl *n*-propyl sulfide (50%). Likely steps in the reaction leading to the aldehyde are shown in the accompanying equations,



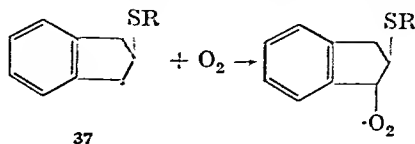
The Oxidative Addition of Thiols to Olefins. When the addition of thiols to olefins is carried out with oxygen supplied to the reaction mixture, oxygen participates in the reaction and the initial product is a β -hydroperoxy sulfide. A probable pathway is shown in the following equations



The hydroperoxide usually rearranges in the reaction mixture to the isomeric β -hydroxy sulfoxide, and this is the major product isolated. The corresponding β -hydroxy sulfide, the conventional thiol-olefin adduct, and the disulfide derived from the thiol are often obtained as by-products. The products isolated from the reaction of *n*-propanethiol, styrene, and oxygen are shown in the accompanying equation.¹¹¹

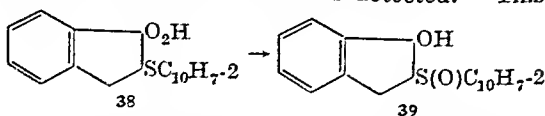


Reduction of the crude hydroperoxide from the reaction of indene, thiophenol, and oxygen gives *trans*-2-phenylmercapto-1-indanol, indicating that the peroxide has the *trans* configuration and that the attack by oxygen on the intermediate radical **37** occurs *trans* to the RS group.¹⁵⁷ Re-



arrangement of this hydroperoxide to the hydroxy sulfoxide gave the two isomers of *trans*-2-phenylsulfinyl-1-indanol.

The initially formed hydroperoxide **38** from the reaction of indene, 2-naphthalenethiol, and oxygen has been isolated in crystalline form (m.p. 70°), characterized,^{158,159} and its decomposition to 2-(2-naphthylsulfinyl)-1-indanol (**39**) in benzene solution observed. When the decomposition was carried out in the presence of 2-(4-chlorophenylmercapto)-1-indanol, no oxidation of the indanol was detected. This observation



suggests that the conversion of **38** to **39** is an intramolecular rearrangement.¹⁵⁹ On the other hand, the crude hydroperoxide from thiophenol, indene, and oxygen is reported to rearrange to the sulfoxide by a second-order process,¹⁵⁷ suggesting an intermolecular oxidation analogous to the well-known bimolecular hydroperoxide oxidation of sulfides to sulfoxides.^{160,161}

The reaction to give β -hydroxy sulfoxides is reported to be strongly accelerated by ehloride and bromide salts.^{162,163} Particularly effective are amine hydrochlorides and hydrobromides, but sodium and potassium bromides and ehlorides are also effective. Iodides are inhibitory. The mechanism of this catalysis is not clear. Ultraviolet radiation has been used to initiate oxidative additions of *n*-dodecanethiol.¹⁵⁹

When the reaction of indene, thiols, and oxygen is carried out in the presence of alkyl amines, hydroxy sulfides and not sulfoxides are obtained,

¹⁵⁷ Ford, Pitkethly, and Young, *Tetrahedron*, **4**, 325 (1958).

¹⁵⁸ Oswald, *J. Org. Chem.*, **24**, 443 (1959).

¹⁵⁹ Oswald, *J. Org. Chem.*, **26**, 842 (1961).

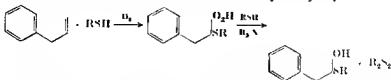
¹⁶⁰ Overberger and Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953).

¹⁶¹ Reid, *Organic Chemistry of Bivalent Sulfur*, Vol. II, pp. 64-66, Chemical Publishing Co., Inc., New York, 1960.

¹⁶² Brederick, Wagner, Kottenhahn, *Chem. Ber.*, **93**, 2415 (1960).

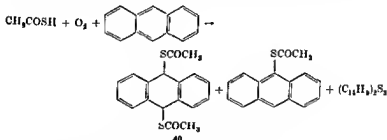
¹⁶³ Brederick, Wagner, and Kottenhahn, *Angew. Chem.*, **70**, 73 (1958).

presumably by intermediate formation of hydroperoxy sulfides followed by amine-catalyzed oxidation of additional thiol by the hydroperoxide¹⁶⁴



The scope of the oxidative addition of thiols to olefins has barely been explored. Both alkanethiols and aromatic thiols have been used. The olefins thus far used include styrene,^{159,162} indene,¹⁵⁹ methacrylonitrile,¹⁶² methyl acrylate,¹⁶² 1-hexene,¹⁶⁵ 1-octene,¹⁶¹ bicyclopentadiene,¹⁶⁶ and Abirin.¹⁶⁶

A related group of oxidative additions are the reactions of thiols with oxygen and anthracene or substituted anthracenes. The principal products are 9,10-dihydro-9,10-disubstituted anthracenes.¹⁶⁷⁻¹⁶⁹ For example, thioacetic acid, oxygen, and anthracene give as the major products two isomeric 9,10-dihydro-9,10-di(acetylthio)anthracenes (40), along with 9-(acetylthio)anthracene and a small amount of di-(9-anthryl)disulfide.¹⁶⁹



It has been postulated that all these products arise from an initially formed hydroperoxide 41¹⁶⁹ (see formula at top of p. 188).

Acetylenes. The radical addition of thiols to acetylenes with a variety of substituents (e.g., alkyl, aryl, carboxyl, α -hydroxyalkyl, α -haloalkyl, alkoxy, and alkylthio) proceeds readily to give monoadducts, diadducts, or both, depending on the relative proportions of the starting materials.

¹⁶⁴ Oswald, Noel, and Fisk, *J. Org. Chem.*, **26**, 3974 (1961).

¹⁶⁵ Harman, U.S. pat. 2,515,129 [*C.A.*, **44**, 8942 (1950)].

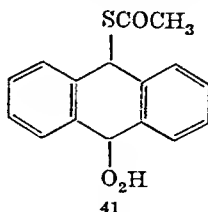
¹⁶⁶ Oswald and Noel, *J. Org. Chem.*, **26**, 3948 (1961).

¹⁶⁷ Mikhaïlov and Blokhina, *Doklady Akad. Nauk SSSR*, **80**, 373 (1951) [*C.A.*, **46**, 5025 (1952)].

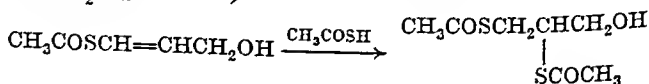
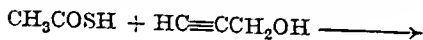
¹⁶⁸ Mikhaïlov and Blokhina, *Probl. Mekhanizma Org. Reaktsii Akad. Nauk, Ukr. SSR, Otdel. Fiz.-Mat. i Khim. Nauk*, **1953**, 215 [*C.A.*, **50**, 14735 (1955)].

¹⁶⁹ Beckwith and Low, *J. Chem. Soc.*, **1961**, 1304.

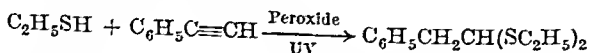
Generally, the first molecule of thiol adds more readily than the second. Only monoadducts are obtained from dimethyl acetylenedicarboxylate and ethanethiol,¹⁷⁰ *p*-methoxyphenylacetylene and thiolacetic acid,¹⁷¹



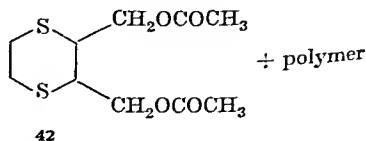
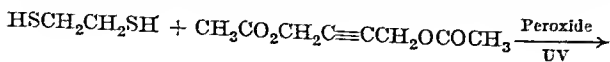
3-methyl-3-hydroxy-1-butyne ethyl ether and ethanethiol,¹⁷² and 4-hydroxy-1-pentyne¹⁷³ or phenylacetylene and thiolacetic acid.¹⁷¹ Addition of the first molecule of thiol proceeds in the anti-Markownikoff manner, forming the abnormal product. The second molecule of thiol generally adds to yield the diadduct with the thio groups on adjacent carbon atoms.^{170,174,175} Additions to phenylacetylene, however, lead to



products in which both RS groups are attached to the β -carbon atom, presumably because of the large resonance stabilization possible in the intermediate benzyl-type radicals.¹⁷⁰



The reaction of ethanedithiol with 2-butyne-1,4-diol diacetate involves cyclization and yields 1,2-bis-(acetoxymethyl)-1,4-dithiane (42) in addition to polymer.¹⁷⁰



¹⁷⁰ Blomquist and Wolinsky, *J. Org. Chem.*, **23**, 551 (1958).

¹⁷¹ Bader, Cross, Heilbron, and Jones, *J. Chem. Soc.*, **1949**, 619.

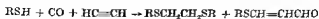
¹⁷² Weiland and Arens, *Rec. Trav. Chim.*, **75**, 1358 (1956).

¹⁷³ Bader, *J. Chem. Soc.*, **1956**, 116.

¹⁷⁴ Yamagishi, Tanaka, and Hoshino, *Bull. Chem. Soc. Japan*, **30**, 455 (1957) [*C.A.*, **52**, 8952 (1958)].

¹⁷⁵ Sauer, *J. Am. Chem. Soc.*, **79**, 5314 (1957).

The peroxide-initiated reactions of acetylene with carbon monoxide and thiols lead to the formation of bis-sulfides and aldehydes, in a manner analogous to the corresponding olefin reaction discussed on p 185¹⁷⁵



Experimental Conditions. Conditions used in radical thiol additions are usually defined by the initiator employed. Peroxides are the most widely employed initiators. Often the peroxides present in the olefin are sufficient to initiate the reaction, possibly by a redox reaction with the thiol. For example, in many addition reactions of thioglycolic acid and thiophenol, an exothermic reaction ensues upon mixing the reactants. The peroxides used include ascaridole, benzoyl peroxide, di-*t*-butyl peroxide, and potassium persulfate.¹⁴⁵

The mixture of reactants, containing the catalyst in amounts varying from a few tenths of a per cent to a few per cent, is usually heated to the decomposition temperature of the catalyst either in an open vessel or, in the case of volatile reactants, in a sealed metal or glass container. In some reactions the peroxides are decomposed by ultraviolet irradiation.^{69,119,170,172,176}

Inorganic reducing agents, e.g., ferrous chloride and chromous chloride, have also been employed to decompose peroxides (redox systems), thus initiating addition at room temperature.¹⁷⁷ Redox systems comprising persulfate and bisulfite have been used extensively in the reactions of dithiols with dienes to produce polymers.¹⁵⁰ Oxygen in small amounts has been employed for initiation¹⁷⁸⁻¹⁸⁰ and may actually be the initiator in many additions reported to occur spontaneously when no precautions are taken to exclude air. When substantial quantities of oxygen are made available to the reaction mixture, oxygen-containing products are formed. Azonitriles, e.g., azobis(isobutyronitrile), have also been employed extensively to catalyze thiol additions, and the conditions are analogous to those used in peroxide-catalyzed reactions. The initiators are generally decomposed thermally, and less frequently by ultraviolet radiation.^{174,181}

Several forms of radiant energy, e.g., ultraviolet radiation, x-rays, γ -rays and β -rays, have been used for initiating thiol addition reactions. Ultraviolet radiation (below 3000 Å) is most commonly used. Initiation by ultraviolet radiation probably can also occur by the photodecomposition

¹⁷⁵ Ruhlmann, Schrapler, and Grasser, *J. Prakt. Chem.*, [4] 10, 325 (1960).

¹⁷⁷ Hoeffelman and Berkenbosch, U.S. pat. 2,352,435 [*C.A.*, 38, 5506 (1944)].

¹⁷⁸ Ellingboe, U.S. pat. 2,423,641 [*C.A.*, 42, 3774 (1948)].

¹⁷⁹ Shostakovskii, Prilezhneva, and Uvarova, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1954, 447.

¹⁸⁰ Vesterman and Frenkel, *Fr. pat.* 1,103,762 [*C.A.*, 52, 18220 (1958)].

¹⁸¹ Theobald, U.S. pat. 2,675,392 [*C.A.*, 49, 4722 (1955)].

of peroxides contained in the reactants, and this may be the mechanism for initiation by radiation of wavelengths greater than 3000 Å. The reactants generally are contained in sealed or open transparent vessels and exposed to an ultraviolet source at ambient temperature. With very low-boiling reactants, e.g., fluoroolefins, irradiation of the reactants at reflux has been employed.⁶ Generally, radiation of 3000 Å or lower is employed, necessitating the use of Vycor or quartz containers. However, many reactions have been reported to proceed in a satisfactory manner when a commercial sunlamp and Pyrex equipment are used.

Ultraviolet radiation above 3000 Å has frequently been used in conjunction with photosensitizers such as acetone,¹⁸² mercury salts,^{183,184} organic disulfides,^{90,109,185-187} and lead tetraalkyls.¹⁸⁸ X-rays have been used to initiate additions of thiols to fluoroolefins,⁶ and both x-rays and γ -rays have been employed in the addition of *n*-butanethiol to 1-pentene.^{72,73} In these reactions the reactants, contained in stainless steel pressure vessels or Pyrex tubes, were exposed to x-rays or γ -rays at ambient temperatures for periods of several hours. β -Radiation from an Sr^{90} . Y^{90} source has been employed to initiate the reaction of *n*-butanethiol and 1-octene contained in a Pyrex reactor.⁷⁴

In the formation of polymers from dithiols and non-conjugated olefins, emulsion polymerization techniques employing exactly equimolecular amounts of the reactants and a bisulfite-persulfate-copper initiator system have given products having the highest molecular weights.^{154,155} Other initiators, e.g., peroxides, azonitriles, and ultraviolet radiation, have also been studied.

Oxidative additions of thiols to olefins are generally carried out by shaking the reactants in a hydrocarbon solvent in an atmosphere of oxygen or with air bubbling through at ambient temperatures.^{111,157} Periods of time vary from an hour to several days. In experiments with anthracene when oxygen absorption was slow, catalytic quantities of cumene hydroperoxide and ferrous sulfate were added.¹⁶⁹ When it is desired to stop the reaction at the hydroperoxide stage, the reactions are preferably carried out at 0° for a few hours.¹⁵⁹ The amine hydrohalide-catalyzed experiments are carried out in essentially the same manner except that a per cent or less of dibutylamine hydrochloride or hydrobromide is added.¹⁶²

¹⁸² Barnard, Fabian, and Koeh, *J. Chem. Soc.*, 1949, 2442.

¹⁸³ Kaneko and Mii, *J. Chem. Soc. Japan*, 59, 1382 (1938) [*C.A.*, 33, 2106 (1939)].

¹⁸⁴ Yamagishi, Tanaka, and Hoshino, *Bull. Chem. Soc. Japan*, 29, 447 (1956).

¹⁸⁵ Rueggeberg, Cook, and Reid, *J. Org. Chem.*, 13, 110 (1948).

¹⁸⁶ Ellingboe, U.S. pat. 2,439,203 [*C.A.*, 42, 5046 (1948)].

¹⁸⁷ Rueggeberg and Cook, U.S. pat. 2,810,687 [*C.A.*, 52, 3850 (1958)].

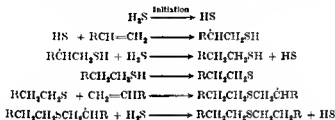
¹⁸⁸ Evans, Vaughan, and Rust, U.S. pat. 2,411,961 [*C.A.*, 41, 2068 (1947)].

Addition of Hydrogen Sulfide to Olefins

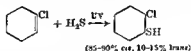
In the presence of ultraviolet radiation or certain free radical initiators, hydrogen sulfide adds to olefins in the abnormal manner to yield mixtures of thiols and sulfides



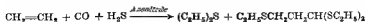
Although no detailed study of the mechanism has been made, it seems certain that these reactions occur via a radical chain mechanism fully analogous to that substantiated for thiol additions. In the products



whose structures have been determined, the SH group is found on the carbon atom normally attacked by radicals, e.g., the terminal carbon in terminal olefins. Formation of the sulfide occurs by a typical thiol-olefin addition reaction. As in thiol additions, the photoinitiated addition of hydrogen sulfide to 1-chlorocyclohexene is predominantly *trans*, the 1:1 adduct consisting of 85-90% *cis*-2-mercapto-1-chlorocyclohexane.⁹⁷ Other aspects of the mechanism and stereochemistry have apparently not been investigated.

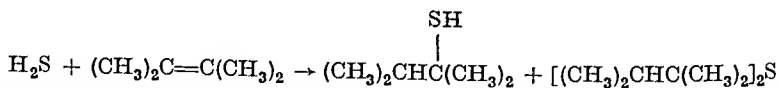


Radical addition of hydrogen sulfide to olefins is a general reaction applicable to terminal, internal, and cyclic olefins. Ethylene and hydrogen sulfide, at temperatures of 160-200° and pressures of 500-1000 atm, react to form a mixture of ethanethiol, diethyl sulfide, and ethyl butyl sulfide.¹⁸² In an azonitrile-initiated reaction of hydrogen sulfide, carbon monoxide, and ethylene, the hydrogen sulfide added to ethylene to give ethanethiol, which was subsequently converted to diethyl sulfide and 2-ethylmercaptopropionaldehyde dithioacetal⁸¹

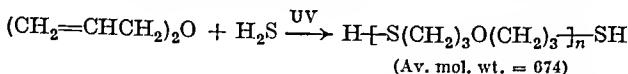


¹⁸² Harmon, U.S. pat. 2,390,099 [C.A., 40, 1865 (1949)]

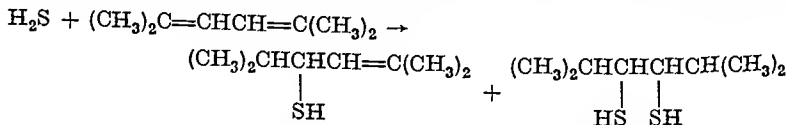
Terminal olefins are the most reactive in radical hydrogen sulfide additions, but highly branched internal olefins, e.g., 2,3-dimethyl-2-butene, also react.¹⁹⁰ Reactions of equimolecular amounts of hydrogen



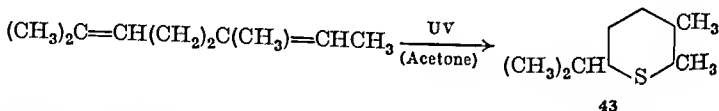
sulfide and dienes such as diallyl ether lead to polymers of low molecular weight.¹⁹¹ With an appreciable excess of hydrogen sulfide, both a



monothiol and dithiols are obtained from bicyclo[2.2.1]hepta-2,5-diene¹⁹² and 2,5-dimethyl-2,4-hexadiene.¹⁹³ The reaction of hydrogen sulfide



with 3,7-dimethyl-2,6-octadiene gave, in addition to two monothiols and a dithiol, a thiopyran 43 resulting from intramolecular sulfide formation.¹⁹⁴



Additions of hydrogen sulfide to ethylenes with hetero atom substituents such as Cl, SiR₃, SR, OR, or NR₂ generally lead to products with the sulfur atom attached to the CH₂ group. Additions to vinyl ethers have been the most extensively examined.¹⁹⁵ In a study of the oxygen-initiated addition of hydrogen sulfide to ethyl, isopropyl, isobutyl, isopentyl, *n*-octyl, and cyclohexyl vinyl ether, the rate of addition was observed to decrease as the alkyl group became longer and more branched.^{196,197} From all the olefins except cyclohexyl vinyl ether, both the thiol and the

¹⁹⁰ Pinkney, U.S. pat. 2,551,813 [C.A., 45, 9559 (1951)].

¹⁹¹ Vaughan and Rust, *J. Org. Chem.*, 7, 472 (1942).

¹⁹² Mahan and Louthan, U.S. pat. 3,019,267 [C.A., 56, 12774 (1962)].

¹⁹³ May and Lee, U.S. pat. 2,960,538 [C.A., 55, 9280 (1961)].

¹⁹⁴ Naylor, *J. Chem. Soc.*, 1947, 1532.

¹⁹⁵ Shostakovskii, Shapiro, and Dubrova, *J. Gen. Chem. USSR (Engl. Transl.)*, 28, 3337 (1958).

¹⁹⁶ Shostakovskii, Prilezhaeva, and Shapiro, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1954, 235.

¹⁹⁷ Shostakovskii, Prilezhaeva, and Shapiro, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1954, 245.

Generally speaking, if a high yield of the thiol is desired, a high ratio of hydrogen sulfide to olefin is necessary. Conversely, for a high yield of sulfide the ratio of olefin to hydrogen sulfide should be high. It has been reported that the presence of water increases the ratio of thiol to sulfide,

TABLE VII
ASCARIDOLE-INITIATED ADDITION OF HYDROGEN
SULFIDE TO *n*-BUTYL VINYL ETHER

Molar Ratio of $\text{H}_2\text{S}:\text{Olefin}$	Ratio of Yield Thiol:Sulfide
0.37	0.081
1.55	1.9
1.98	3.5
2.13	5.6

other factors being constant.²⁰¹ The polymer from hydrogen sulfide and diallyl ether has the highest molecular weight when an exact 1:1 ratio of reactants is used.²⁰²

The choice of initiator in radical additions of hydrogen sulfide to olefins is more critical than in thiol additions. Ultraviolet radiation was used initially, and it is still one of the best methods.¹⁹¹ Hydrogen sulfide absorbs below about 2800 Å and is dissociated into hydrogen atoms and $\cdot\text{SH}$ radicals by such radiation.²⁰³ As in thiol-olefin additions, radiation of wavelength longer than 3000 Å can be used if a photosensitizer, such as acetone, tetraethyllead, or a mercury salt, is added. γ -Radiation²⁰⁴ and x-rays^{199a} have also been employed.

Peroxides are of limited usefulness as initiators, possibly because they enter into an oxidation-reduction reaction with hydrogen sulfide to produce sulfur, which is a good inhibitor of radical chain reactions. In studies with *n*-butyl vinyl ether, it was found that benzoyl peroxide, hydrogen peroxide, and the peroxides formed on long contact of the ether with air actually inhibit the radical addition and sometimes accelerate the ionic addition. The inhibition is probably to be ascribed to the formation of acidic substances.¹⁹⁶ On the other hand, ascaridole at 1% concentration initiated the addition smoothly. Ascaridole, however, did not initiate the addition of hydrogen sulfide to isopentyl vinyl ether.¹⁹⁷ Di-*t*-butyl peroxide has been reported to be effective for the reaction of diallyl ether with hydrogen sulfide to give polymer,²⁰⁵ and, when combined with iron, an effective initiator for the addition to 2,5-dimethyl-2,4-hexadiene

²⁰¹ May, Ridgway, and Wadsworth, U.S. pat. 2,865,965 [*C.A.*, 53, 10001 (1959)].

²⁰² Vaughan and Rust, U.S. pat. 2,522,589 [*C.A.*, 45, 455 (1951)].

²⁰³ Ramsay, *J. Chem. Phys.*, 20, 1920 (1952).

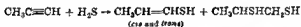
²⁰⁴ Dow Chemical Co., Brit. pat. 842,277 [*C.A.*, 55, 5346 (1961)].

²⁰⁵ McMillan, U.S. pat. 2,514,661 [*C.A.*, 44, 9184 (1950)].

to give a mono- and a di-thiol.¹⁹³ Benzoyl peroxide has been used in the addition to di-*n*-butyl α -methyl- α' -methyleneadipate.²⁰⁶ Traces of oxygen initiate the addition of hydrogen sulfide to vinyl ethers¹⁹⁶ and vinyl sulfides,¹⁷⁹ but larger amounts (e.g., 0.05% in the case of butyl vinyl ether) are inhibitory.¹⁹⁶ Of all the radical initiators studied, azonitriles seem to be the most satisfactory for hydrogen sulfide additions.^{190,200}

Ionic additions of hydrogen sulfide to olefinic hydrocarbons have been effected with many catalysts; e.g., sulfur, sulfuric acid, Friedel-Crafts catalysts, alumina, metal sulfides and polysulfides, and silica. These reactions lead to products with normal (Markownikoff) orientation except that some high-temperature reactions catalyzed by metal sulfides furnish both normal and abnormal adducts.²⁰⁷ Ionic additions to α,β -unsaturated carbonyl compounds and nitriles have been catalyzed by alkoxides, amines, and sodium acetate, and the formation of α -mercaptoethyl ethers by addition to vinyl ethers has been catalyzed by acids. Reviews of hydrogen sulfide additions to olefins have been given by Knunyants and Fokin⁷⁰ and Naylor.^{184,208}

The x-ray-initiated reaction of hydrogen sulfide (in excess) with a series of mono- and disubstituted acetylenes led to the formation of vinyl thiols in addition to other products.^{209a} For example, from propyne, both the *cis* and *trans* isomers of 1-propene-1-thiol were obtained along with 1,2-dimercaptopropane and polymeric oil. Similar results were obtained



with 3,3,3-trifluoropropyne, 2-butyne, and hexafluoro-2-butyne, except that in the last mentioned case a single isomer of hexafluoro-2-butene-2-thiol (43a) was obtained. From phenylacetylene the major product



was bis-(β -phenylvinyl)sulfide (43b).

Experimental Conditions. Ultraviolet-initiated reactions have been carried out by irradiating the reactants in a vessel cooled to -80° with the ultraviolet source immersed directly in the mixture,⁹⁷ or in sealed quartz tubes cooled in a transparent liquid in a quartz container with an external ultraviolet source.¹⁹¹ Ultraviolet sources radiating at 2537 Å

¹⁹³ Bortnick and Fegley, French pat. 1,218,412 (1960).

¹⁹⁷ Barr and Keyes, *Ind. Eng. Chem.*, **26**, 1111 (1934).

¹⁹⁸ Naylor, *J. Polymer. Sci.*, **1**, 305 (1946).

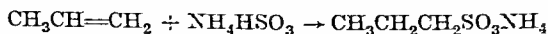
^{209a} Stacey and Harris, *J. Am. Chem. Soc.*, **85**, 963 (1963).

(e.g., a Hanovia SC-2537 lamp) are generally used. The times vary from a few minutes, for 1-butene at 0°,¹⁹¹ to several hours, for 1-chlorocyclohexene at -78°. ⁹⁷ Temperatures ranging from -78° to room temperature have been used. Temperature effects have been noted. The addition of 1-butene at 0° proceeded in 89% conversion while at -78° the conversion was 40-45%.¹⁹¹ Pyrex vessels can be used in experiments employing sensitizers (generally acetone) and ultraviolet sources radiating at or above 3000 Å. Additions to vinyl silanes have been accomplished by irradiating the refluxing silane while hydrogen sulfide was bubbled through.²⁰⁹ Ultraviolet-initiated additions have been carried out in the gas phase, but they are much slower than in the liquid phase.

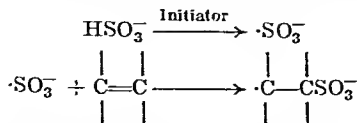
In azonitrile-initiated experiments, α, α' -azo-bis(isobutyronitrile),^{190,200} 1,1'-azo-bis(cyclohexanecarbonitrile),¹⁹⁰ and α, α' -azo-bis(α, γ -dimethylmaleonitrile)¹⁹⁰ in amounts varying from a few tenths of 1% to a few per cent have been used. Generally the reactants are sealed in glass²⁰⁰ or metal¹⁹⁰ vessels without a solvent and are heated for a period of a few hours to 60 hours at catalyst decomposition temperatures. In peroxide-initiated experiments, ascaridole (1%),¹⁹⁶ di-*t*-butyl peroxide (5%),²⁰⁵ and a peroxidized dioxane-hydrogen chloride solution¹⁹⁶ have been used, the procedures being analogous to those for azonitrile-initiated experiments. In the oxygen-initiated additions to vinyl ethers, the reactants containing 0.01% or less of oxygen are sealed in glass vessels and allowed to stand at room temperature for several days.¹⁹⁶

Addition of Bisulfite Ion to Olefins and Acetylenes*

Bisulfite ion in aqueous solution adds in the anti-Markownikoff sense to olefins and acetylenes in the presence of certain oxidants or free radical initiators. For example, from propylene and ammonium bisulfite in the presence of oxygen, ammonium *n*-propane-1-sulfonate is obtained.²¹⁰ The free radical chain mechanism for the olefin reaction, originally proposed



by Kharasch and co-workers,²¹¹ may be formulated as follows.

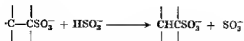


²⁰⁹ Zappel, Ger. pat. 1,000,817 [C.A., 53, 13054 (1959)].

* The addition of bisulfite to olefins has been reviewed by Walling (ref. 45, p. 326) and Mayo and Walling (ref. 8). A summary of the work done before the free radical nature of the reaction was recognized is given by Kharasch, May, and Mayo.²¹⁰

²¹⁰ Kharasch, May, and Mayo, *J. Org. Chem.*, 3, 175 (1938).

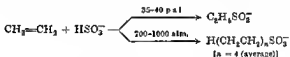
²¹¹ Kharasch, May, and Mayo, *Chem. & Ind. (London)*, 57, 774 (1938).



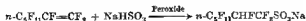
The exact nature of the adding species, represented here as the sulfite ion radical, is not known with certainty; it may well be the bisulfite radical, $\text{HSO}_3^{\cdot -}$.^{*} In any event, the adding species does contain sulfur, since in those products whose structures have been determined the sulfur atom is attached to the carbon atom generally attacked by free radicals.

The reaction has not been studied broadly. No stereochemical studies have been made, and no information concerning the reversibility of the addition step has been obtained. Neither has its scope been clearly defined. For the bisulfite source, sodium, potassium, ammonium, and some amine²¹⁴ bisulfites have been employed. In the majority of examples reported, oxygen was the initiator, either added intentionally or adventitiously. Other oxidants or radical sources such as peroxides,²¹⁵ nitrite, and nitrate²¹⁶ have also been used. In oxygen-initiated additions there occurs a competing oxidation of bisulfite to bisulfate, a disadvantage not inherent in peroxide-initiated reactions.

Both terminal and internal^{216,216} olefins undergo the reaction satisfactorily. With ethylene, either the 1:1 adduct^{216,217} or higher telomers²¹⁸ can be obtained, depending on the ethylene pressure employed. Peroxide-initiated bisulfite addition to fluoroolefins occurs readily, affording a route



to highly fluorinated alkanesulfonic acids.²¹⁸ Other substituted olefins,



including vinyl chloride, allyl alcohol, styrene, vinyl sulfides, vinyl sulfoxides, and vinyl sulfones, also undergo the reaction

* Both the sulfite ion radical and the bisulfite radical have been proposed as intermediates in the autooxidation of bisulfite ion and sulfite ion by oxygen.^{218, 217}

²¹² Bäckström, *Z. Physik. Chem.*, **B25**, 122 (1934).

²¹³ Franck, and Haber, *Sitzber. Preuss. Akad. Wiss. Physik. Math. Kl.*, p. 250 (1931) [*C.A.*, **25**, 4773 (1931)].

²¹⁴ Kharasch, Schenck, and Mayo, *J. Am. Chem. Soc.*, **61**, 3092 (1939).

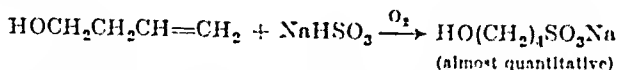
²¹⁵ Kosbar, Troth, and LaZerte, *J. Am. Chem. Soc.*, **75**, 4595 (1953).

²¹⁶ Bohme Fettechemie, Brit. pat., 758,105 [*C.A.*, **51**, 12956 (1957)].

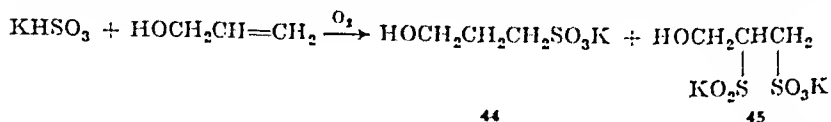
²¹⁷ Koller and Lepworth, *J. Chem. Soc.*, **127**, 307 (1925).

²¹⁸ Hanford, U.S. pat. 2,398,426 [*C.A.*, **40**, 3828 (1946)].

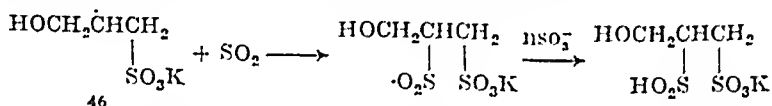
Hydroxyl-substituted olefins, e.g., allyl carbinol,²¹⁶ work particularly well, probably because of their relatively high solubility in the aqueous bisulfite solution.



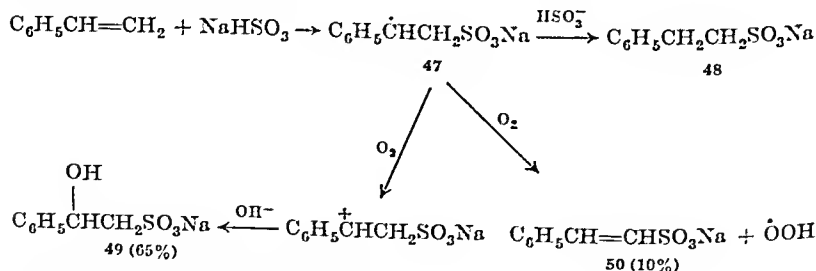
In the oxygen-catalyzed addition of bisulfite ion to allyl alcohol the sole product at pH 7 is the 1:1 adduct 44, but at pH 4 a sulfonate-sulfinate 45 is virtually the exclusive product.²¹⁹⁻²²¹ A possible mechanism for the



formation of 45 is the reaction of the intermediate radical 46 with sulfur dioxide followed by chain transfer with bisulfite ion.



In oxygen-catalyzed addition of bisulfite ion to styrene, two products in addition to the 1:1 adduct 48 are obtained.²¹⁴ They are 2-hydroxy-2-phenylethanesulfonic acid (49), the major product of the reaction, and 2-phenylethylsulfonic acid (50). The three products are not interconvertible under the reaction conditions and presumably arise from the same intermediate radical, the two new products deriving from reactions of this radical with oxygen.



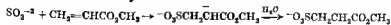
If the oxygen is replaced by nitrite or persulfate, none of the unsaturated sulfonate 50 is formed, presumably because of the inability of these oxidants to remove a hydrogen atom from the intermediate radical 47.

²¹⁹ Helberger, *Angew. Chem.*, **73**, 69 (1961).

²²⁰ Helberger, Ger. pat. 915,693 [*C.A.*, **49**, 10357 (1955)].

²²¹ Helberger, *Ann.*, **588**, 71 (1954).

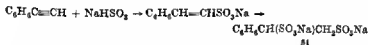
It has been shown conclusively that with ordinary olefins no addition of bisulfite occurs in the absence of an oxidant or other radical-producing source.²¹⁰ On the other hand, bisulfite ion adds very rapidly to α,β -unsaturated carbonyl compounds and nitriles. Since this reaction is completely unaffected by factors which usually promote or retard radical additions, it is obviously ionic in nature.^{221,223}



In the addition of bisulfite ion to acetylenes, both 1:1 and 2:1 adducts are formed.²²⁴ 1-Hexyne yields sodium *n*-1-hexene-1-sulfonate and disodium hexane-1,2-disulfonate. Similarly, from phenylacetylene, both adducts were obtained. The 2:1 adduct is apparently exclusively



disodium 1-phenylethane-1,2-disulfonate **51** in contrast to the diadducts



from the radical addition of thiols to phenylacetylene in which both thiol groups are terminal.¹⁷⁰

Experimental Conditions. Most radical additions of bisulfite ion to olefins and acetylenes have been carried out in aqueous (20–40%) buffered solutions containing an excess of bisulfite with oxygen as the initiator. Many reactions have been carried out at the boiling point with air or oxygen passed through the reaction mixture.^{225,226} Pressure vessels have been used for reactions involving gaseous olefins.

Since oxygen is consumed in the competing autoxidation of bisulfite to bisulfate, a continuous supply of oxygen is necessary to achieve high conversions. The relative amounts of the two products, i.e., bisulfate ion and the addition product, depend largely on the nature of the olefin, its solubility in the reaction mixture, and the ease with which addition takes place. There is an optimum pH (5–7) for the addition reaction; this value varies somewhat with the olefin used and with the cation initially associated with the bisulfite ion employed. Since the autoxidation of bisulfite ion results in an increase in acidity (bisulfate is more acidic than bisulfite),

²²² Schenck and Danzelsky, *J. Org. Chem.*, **16**, 1683 (1951).

²²³ Morton and Landfeld, *J. Am. Chem. Soc.*, **74**, 3523 (1952).

²²⁴ W. J. Wensch, Doctoral Dissertation, New York University, 1955, *Dissertation Abstr.*, **18**, 606 (1958).

²²⁵ I. G. Farbenindustrie, Brit. pat. 454,675 [*C. A.*, **31**, 1430 (1937)].

²²⁶ Ufer, Ger. pat. 681,338 [*C. A.*, **36**, 2052 (1942)].

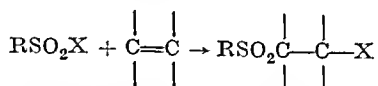
a disadvantageous effect of the concurrent autoxidation is a change in the pH from the optimum, which slows down the addition. This effect can be offset by buffering with sulfite ion, which is oxidized to sulfate ion. Buffering is accomplished by the addition of ammonia when ammonium bisulfite is used as the bisulfite source.²¹⁰

With radical initiators other than oxygen, e.g., benzoyl peroxide, *t*-butyl perbenzoate, and 2,2-bis(*t*-butylperoxy)butane, particularly in solvent systems such as aqueous methanol, aqueous hexanolamine, and aqueous pyridine, yields of alkanesulfonic acid salts in the range 80–100% have been obtained in autoclave reactions.²²⁷ Similarly, the peroxide-initiated addition to fluoroolefins in aqueous borax solution occurs with relatively high yields in autoclaves.²¹⁵

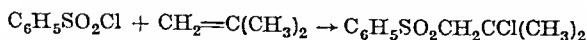
The temperatures employed in experiments with peroxide catalysts are generally those required for decomposition of the catalyst. With oxygen, temperatures between -5° and 100° have been used, room temperature being most common.

Addition of Sulfonyl and Sulfuryl Halides to Olefins

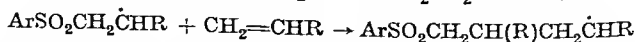
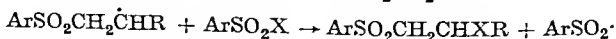
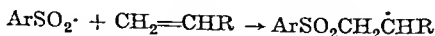
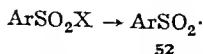
Free radical chain addition to olefins of a variety of compounds containing sulfonyl halide groups, e.g., sulfuryl chloride, sulfuryl chloride fluoride, aromatic sulfonyl halides, and *N*-chlorosulfonylphthalimide, have been reported.



The additions of arylsulfonyl halides to give β -haloalkyl aryl sulfones have



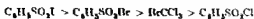
received the most attention, and a typical radical chain mechanism has been proposed.



The arylsulfonyl radical 52 is the adding or chain-carrying species since, in all products whose structures have been determined, the sulfonyl group is attached to the carbon atom generally attacked by radicals. Arylsulfonyl chlorides, bromides, and iodides all undergo the reaction.

²²⁷ Harman, U.S. pat. 2,504,411 [*C.A.*, **44**, 5897 (1950)].

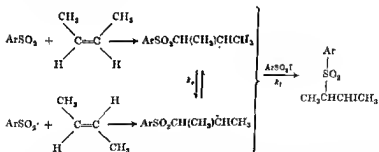
In a study of comparative reactivities of benzenesulfonyl halides and bromotrichloromethane in additions to olefins, the following order was determined.²²⁸ *p*-Chlorobenzenesulfonyl chloride has been reported to



be considerably more reactive than benzenesulfonyl chloride.²²⁹

Both internal and terminal olefins undergo the reaction readily. With ethylene, *p*-chlorobenzenesulfonyl chloride forms a series of telomers in addition to the 1:1 adduct.²²⁹ Substituted olefins, e.g., allyl acetate, methyl acrylate, vinyl bromide, methyl methacrylate, allyl chloride, acrylonitrile, styrene, and 3,3-diacetoxy-1-propene react, and the products obtained are those expected if it is assumed that $\text{ArSO}_2\cdot$ is the adding species.

The stereochemistry of arylsulfonyl halide additions has received some attention. Ultraviolet-catalyzed addition of benzenesulfonyl iodide to either *cis*- or *trans*-2-butene yields the same mixture of diastereomeric addition products under conditions in which the individual olefins are not isomerized.^{230,231} Thus, in a fashion analogous to radical thiol additions, equilibration of the intermediate radical occurs before the transfer step takes place.



The value of $(k_1/k_2)[\text{C}_6\text{H}_5\text{SO}_2\text{I}]$ has been estimated as $\geq 10^4$ in this case.²³⁰

Peroxide- or ultraviolet-initiated addition of *p*-toluenesulfonyl chloride to norbornene occurs *trans*, apparently exclusively, giving *exo*-2-*p*-toluenesulfonyl-*endo*-3-chloronorbornane (53) without rearrangement.^{149,232}

²²⁸ J. H. McNamara, Doctoral Dissertation, Pennsylvania State University, 1956, *Dissertation Abstr.*, 17, 226 (1957).

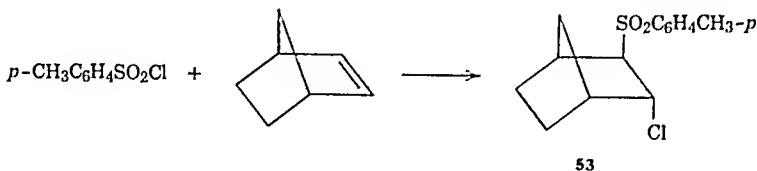
²²⁹ Ladd, U.S. pat. 2,573,560 [C.A., 46, 7588 (1952)].

²³⁰ Skell, Woodworth, and McNamara, *J. Am. Chem. Soc.*, 79, 1253 (1957).

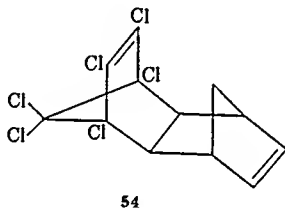
²³¹ Skell and McNamara, *J. Am. Chem. Soc.*, 79, 85 (1957).

²³² Crestel and Reeder, *J. Org. Chem.*, 26, 2162 (1961).

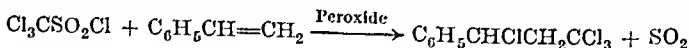
This result is unusual in that radical additions to norbornene generally occur *cis*. Evidently approach of *p*-toluenesulfonyl chloride on the *exo* side of the intermediate radical for transfer is impossible for steric



reasons. Similarly, *trans* addition to *endo-exo*-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (54) without rearrangement was noted.^{149,232} The addition to norbornadiene occurs with rearrangement to give 3-*p*-toluenesulfonyl-5-chloronortriethylene.^{149,232}

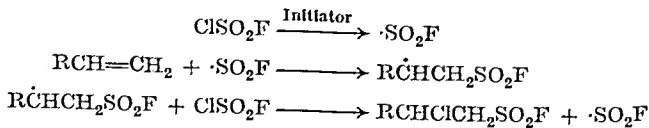


Peroxide-initiated reaction of trichloromethanesulfonyl chloride with styrene leads to addition of the elements of carbon tetrachloride with loss



of sulfur dioxide.²³³ There are apparently no examples of radical additions of alkanesulfonyl halides to olefins.

Peroxide- or ultraviolet-initiated addition of sulfonyl fluoride chloride to olefins results in the formation of chloroalkanesulfonyl fluorides, by a radical chain process.^{234,235}



There is little or no cleavage of the sulfur-fluorine bond. Yields with long-chain terminal olefins, e.g., 1-octadecene, are high; with olefins of low molecular weight, telomers containing 2 and 3 olefin units are obtained

²³³ Ladd and Kiley, U.S. pat. 2,696,213 [*C.A.*, 47, 6440 (1953)].

²³⁴ Tiers, Fr. pat. 1,176,791; U.S. pat. 2,846,472 [*C.A.*, 53, 12175 (1959)].

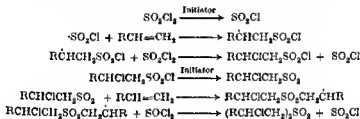
²³⁵ Tiers, Fr. pat. 1,176,792; U.S. 2,846,472 [*C.A.*, 53, 12175 (1959)].

in addition to the 1:1 adduct. With fluorinated ethylenes, chloropolyfluoroalkanesulfonyl fluorides containing an average of 4 to 18 olefin units are formed

The reactions of sulfonyl chloride with terminal olefins in the presence of sulfur dioxide result in the formation of sulfones in 15-30% yields, and of dichloroalkanes in 50-80% yields. One-to-one adducts (sulfonyl chlorides) have not been obtained in these reactions



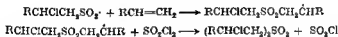
Two mechanisms have been proposed by Kharasch and Zavist^{235,237} The first, a typical chain type involving the intermediate formation of a



sulfonyl chloride which adds to the olefin by a subsequent chain reaction, is unlikely since it was found that an alkane sulfonyl chloride would not add to the olefin under conditions in which sulfones are formed. The second scheme postulates a rearrangement of the intermediate radical⁵⁵



55



with a shift of chlorine from sulfur to the β -carbon atom and thus obviates the necessity for an alkane sulfonyl chlorine-olefin addition. At the present time this mechanism seems the more likely, but further work is necessary to substantiate it.

The only unequivocal example of the formation of an alkane sulfonyl chloride by a radical process from an olefin and sulfonyl chloride is the telomerization of ethylene with sulfonyl chloride.²³⁸ A radical mechanism



has been postulated for the formation of β,β -dichloroethanesulfonyl

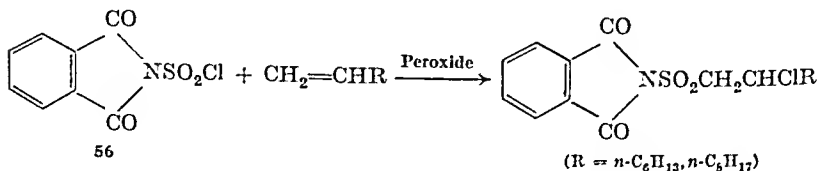
²³⁵ Kharasch and Zavist, *J. Am. Chem. Soc.*, **73**, 564 (1951)

²³⁷ Kharasch and Zavist, *J. Am. Chem. Soc.*, **70**, 3526 (1948)

²³⁸ Hanford and Joyce, U.S. pat. 2,446,860 (*C.A.*, **42**, 6373 (1948))

chloride from a reaction of vinyl chloride and sulfonyl chloride catalyzed by sulfur chlorides,^{236,239} but it seems unlikely that this can be a radical reaction.

Mixtures of N-chlorosulfonylphthalimide (56) and 1-decene or 1-octene react in the presence of peroxide to give N-(chloroalkylsulfonyl)phthalimides, presumably by a chain mechanism analogous to that written for



aromatic sulfonyl halide additions.²⁴⁰ Efforts to effect additions of N-chlorosulfonylphthalimide to styrene, indene, vinyl acetate, or allyl chloride, and of N,N-dimethylsulfamyl chloride and N,N-dimethylcarbamyl chloride to 1-octene, failed.

Experimental Conditions. The additions of aromatic sulfonyl halides and sulfonyl chloride fluoride have been carried out by heating the reactants (in an autoclave if the olefin is low-boiling), at the decomposition temperature of the azonitrile or peroxide catalyst.^{229,235,241} Benzenesulfonyl iodide additions have been accomplished by ultraviolet irradiation of the olefin and the freshly prepared iodide in carbon tetrachloride solution.^{228,231} The additions of sulfonyl chloride to terminal olefins to give sulfones have been carried out by adding a solution of sulfonyl chloride in the olefin to a suspension of benzoyl peroxide in the olefin at 60–65° through which a slow stream of sulfur dioxide is passing. Reaction times are 6–7 hours.^{236,237}

Miscellaneous Additions to Form C—S Bonds

Addition of Sulfenyl Chlorides. Sulfenyl chlorides, which undergo ionic addition to hydrocarbon olefins readily,²⁴² have recently been shown to undergo free radical additions also.^{243–245} Thus trichloromethanesulfenyl chloride has been reported to add to styrene under the influence of benzoyl peroxide or ultraviolet radiation.^{243,244} The product isolated

²³⁹ Yakubovich and Zinov'ev, *J. Gen. Chem. USSR*, **17**, 2028 (1947) [*C.A.*, **43**, 1248 (1949)].

²⁴⁰ Kharasch and Mosher, *J. Org. Chem.*, **17**, 453 (1952).

²⁴¹ Ladd, U.S. pat. 2,521,068 [*C.A.*, **45**, 653 (1951)].

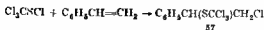
²⁴² Kharasch, Buess, and Strashun, *J. Am. Chem. Soc.*, **74**, 3422 (1952).

²⁴³ Prey, Gutschik, and Berbalk, *Monatsh. Chem.*, **91**, 794 (1960).

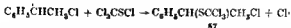
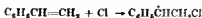
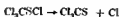
²⁴⁴ Prey and Gutschik, *Monatsh. Chem.*, **90**, 551 (1959).

²⁴⁵ Harris, *J. Am. Chem. Soc.*, **84**, 3148 (1962).

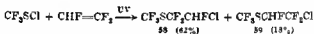
was assigned structure 57, with the chlorine atom on the terminal carbon



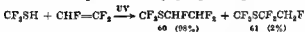
atom indicating that a chlorine atom, rather than the trichloromethylthiyl radical, is the adding species. A chain mechanism has been proposed²⁴³



The ultraviolet- or azonitrile-initiated reaction of trifluoromethanesulfonyl chloride with several unsymmetrical fluoroolefins has yielded both possible 1:1 adducts.²⁴⁵ For example, from the reaction with trifluoroethylene, both 58 and 59 were obtained. In previously studied radical additions of trifluoromethanethiol, hydrogen bromide, and trifluoromethyl iodide to trifluoroethylene, two 1:1 adducts have also



been obtained. The predominant isomer results from attack by the chain-carrying radical on the monofluorinated carbon atom. Thus, in the addition of trifluoromethanethiol, 60 is the predominant product. Since the orientation with respect to the CF_3S group of the predominant adduct



(58) obtained in the sulfonyl chloride reaction is just opposite to that (60) obtained in the corresponding thiol addition, it appears that in this case also the predominant adding species must be the chlorine atom. Several other examples of trifluoromethanesulfonyl chloride additions have been studied and, where a direct comparison with the analogous trifluoromethanethiol addition was made, it was found that the orientation with respect to the trifluoromethylthio group was reversed (Table VIII)

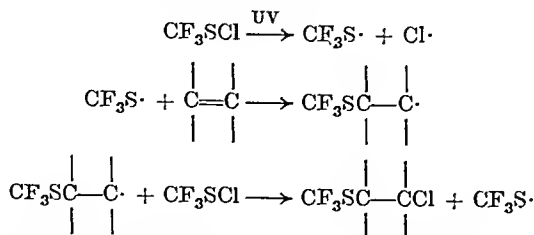
TABLE VIII

COMPARISON OF COMPOSITION OF 1:1 ADDUCT FRACTIONS FROM CF_3SCl AND CF_3SH RADICAL ADDITIONS

The numbers represent the % composition of the 1:1 adduct fraction with respect to the orientation of the CF_3S group.)

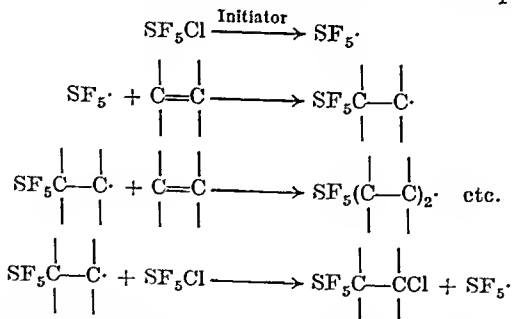
	$\text{CH}_2=\text{CHCl}$		$\text{CF}_2=\text{CHF}$		$\text{CF}_2=\text{CFCI}$		$\text{CF}_2=\text{CH}_2$	
CF_3SCl	5	95	32	18	25	75	78	22
CF_3SH	100	0	2	98	100	0	0	100

Since in each of the sulfenyl chloride additions both 1:1 adducts are obtained, it appears that the reaction is also occurring, to some extent at least, by a mechanism analogous to the thiol mechanism involving the CF_3S radical as the chain-carrying species.

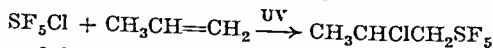


Ultraviolet- or peroxide-initiated additions of trichloromethanesulfonyl chloride to cyclohexene,^{243,244} 1-hexene,²⁴³ 1-octene,²⁴³ allyl acetate,²⁴³ allyl chloride,²⁴³ indene,²⁴⁴ benzofuran,²⁴⁴ and hexachlorodihydrothiophene²⁴⁴ have also been carried out, but no pertinent structural data on the products have been reported.

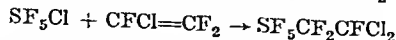
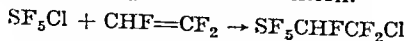
Addition of Sulfur Chloride Pentafluoride. Recently radical additions of sulfur chloride pentafluoride (SF_5Cl) to olefins and acetylenes have been reported and a radical chain mechanism has been proposed.²⁴⁶⁻²⁴⁹



The ultraviolet-initiated addition to propylene yields 2-chloropropyl sulfur pentafluoride, indicating that the SF_5 radical is the adding species.



The orientation of the 1:1 adducts in additions to chlorotrifluoroethylene and trifluoroethylene also support this contention.



²⁴⁶ Case, Ray, and Roberts, *Proc. Chem. Soc.*, 1960, 401.

²⁴⁷ Roberts, *Quart. Rev. (London)*, 15, 40 (1961).

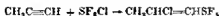
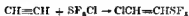
²⁴⁸ Case, Ray, and Roberts, *J. Chem. Soc.*, 1961, 2066.

²⁴⁹ Case, Ray, and Roberts, *J. Chem. Soc.*, 1961, 2070.

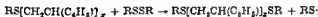
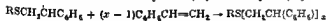
With tetrafluoroethylene in the presence of a free radical initiator, a series of telomers **62** is formed. When the reaction is initiated with ultraviolet radiation, a second series of telomers **63** is formed in addition



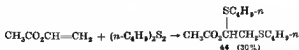
to the series **62**. Additions to ethylene, butadiene, and cyclohexene have also been carried out. Isobutylene and styrene polymerize in the presence of sulfur chloride pentafluoride and apparently do not yield 1:1 adducts. Additions to acetylene and methyl acetylene give only 1:1 adducts



Addition of Disulfides. *Organic Disulfides.* Organic disulfides have been examined extensively as chain transfer agents in free radical vinyl polymerizations, and studies of the polymerization of styrene in the presence of disulfides have shown that the polymers contain two RS groups per molecule (ref. 45, pp. 156-157, 332-333)



The magnitudes of disulfide-olefin transfer constants indicate that 1:1 chain addition of the more reactive disulfides to olefins should be possible. Apparently, the only such reaction reported is the photoinitiated addition of *n*-butyl disulfide to vinyl acetate to give 1,2-bis(*n*-butylthio)ethyl acetate (**64**)⁷⁶. It is not known whether this product is formed by a chain-propagating displacement step or by the addition of two RS radicals



produced by photolysis of the disulfide. Disulfide-olefin additions catalyzed by iodine have been reported, but these are ionic in nature.^{250 251 252}

Thiocyanogen. Although a large number of additions of thiocyanogen to carbon-carbon double and triple bonds have been recorded²⁵² and

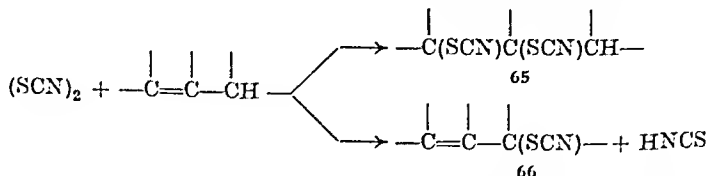
²⁵⁰ Holmberg, *Arkiv Kemi Mineral. Geol.*, **13B**, No. 14 (1939)

²⁵¹ Schneider and Bagnell, *J. Org. Chem.*, **26**, 1994 (1961).

²⁵² Schneider, Bagnell, and Murdoch, *J. Org. Chem.*, **26**, 1987 (1961)

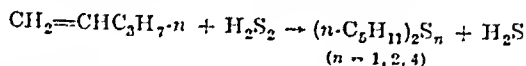
²⁵³ Wood, in Adams, *Organic Reactions*, Vol. 3, Chap. 6, John Wiley & Sons, New York,

although it has been noted that the reactions are accelerated by ultraviolet radiation, there has been very little study of the mechanism of the reaction. Quite recently, it was reported that the reaction is also influenced by the presence of peroxides, and a free radical mechanism was proposed.²⁵³ Addition to the double bond to give 65 may be accompanied by allylic substitution to give 66. The relative amounts of addition and substitution depend on the structure of the olefin. Cyclo-



hexene undergoes both addition and substitution, whereas 1-methylcyclohexene undergoes largely substitution and 1-octene exclusively addition. In view of the scanty literature on the free radical nature of thiocyanogen additions, and the fact that there is available a tabulation of many examples,²⁵² no further review will be presented in this chapter.

Hydrogen Disulfide. The decomposition of hydrogen disulfide in the presence of an excess of an olefin results in the formation of monosulfides, disulfides, and tetrasulfides. For example, from 1-pentene at 50°, diamyl monosulfide, diamyl disulfide, and diamyl tetrasulfide were obtained in yields of 31%, 12%, and 25%, respectively.^{254,255}



The decomposition of hydrogen disulfide to sulfur and hydrogen sulfide is a competing reaction and becomes of major importance with less reactive olefins. Thus the yield of hydrogen sulfide increased from 4–5% with 1-pentene to 21% with 2-pentene, and to 30% with cyclohexene. Other olefins which have been tried in this reaction, but for which products have not been disclosed, include styrene, isoprene, and α -methylstyrene.

A chain mechanism with an initiation step involving scission of the S—S bond of hydrogen disulfide has been proposed to account for the products formed.²⁵⁵ However, the structures of the products have

apparently not been determined, and more research is necessary to establish that the reactions proceed by way of a free radical mechanism

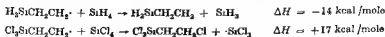
ADDITION OF SILANES TO OLEFINS AND ACETYLENES

The synthesis of organosilicon compounds by adding to olefins silanes containing one or more Si—H bonds was first reported in 1947 by three groups of investigators Sommer, Pietrusza, and Whitmore²⁵⁶ and Burkhard and Krieble²⁵⁷ reported independent studies of the peroxide-initiated additions of trichlorosilane. The former group also noted the ultraviolet-initiated addition of trichlorosilane to 1-octene, and the latter workers included methyldichlorosilane and a rather wide variety of unsaturates in their study. The third paper, by Barry, DePree, Gilkey, and Hook,²⁵⁸ reported the thermal, uncatalyzed addition of silanes to olefins under pressure. Subsequently a substantial amount of research on the radical addition of silanes to unsaturates appeared in published papers and in the patent literature. Concurrently, ionic additions, catalyzed by metals and metal salts (e.g., platinum and potassium chloroplatinate) have been found and explored extensively.

This discussion and the accompanying tables are concerned only with the free radical addition. The metal and metal salt-catalyzed reactions, which are the subject of a considerable body of literature, are excluded. A recent report states that iron pentacarbonyl catalyzes the free radical addition of silanes to olefins. Although there is room for doubt concerning the mechanism of reaction with this catalyst, examples are included in the tables.

Mechanism; Scope and Limitations

The free radical chain addition of silanes to olefins and acetylenes occurs only with compounds having one or more hydrogen atoms attached to silicon. This fact and its corollary, the failure to observe additions involving Si—X bonds (X = Cl or Br), can be accounted for by the energetics of the respective displacement steps⁴⁵

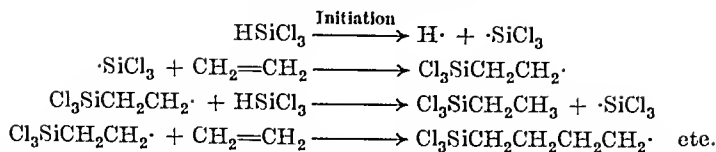


The mechanism of the reaction is illustrated for the addition of trichlorosilane to ethylene

²⁵⁶ Sommer, Pietrusza, and Whitmore, *J. Am. Chem. Soc.*, **69**, 188 (1947).

²⁵⁷ Burkhard and Krieble, *J. Am. Chem. Soc.*, **69**, 2687 (1947).

²⁵⁸ Barry, DePree, Gilkey, and Hook, *J. Am. Chem. Soc.*, **69**, 2216 (1947).



The formulation of the initiation step depends, of course, on the nature of the initiator. Radiation or thermal initiation probably proceeds as shown. With peroxides or other chemical initiators, initiation should probably be written to indicate abstraction of the hydrogen atom from trichlorosilane by an initiator fragment.

Addition has been initiated in a variety of ways, including exposure to ultraviolet^{256,259} or ionizing radiation,²⁶⁰ heating at 160–400° in the absence of any added catalyst,²⁵⁸ and heating in the presence of peroxides^{256,257} or azo compounds.^{261,262} The peroxides used most frequently as initiators are acetyl peroxide, *t*-butyl perbenzoate, di-*t*-butyl peroxide, and, especially, benzoyl peroxide. A study has been made of the influence of a wide variety of substances on the *t*-butyl perbenzoate-catalyzed addition of trichlorosilane to 1-pentene.²⁶³ Tin promotes the reaction, apparently through an induced decomposition of the peroxide, and with a mixture of tin and stannic chloride the reaction is violent even at room temperature. Such substances as alcohol, nickel, lead, zinc, traces of water and silicone grease are without significant effect, while iron and iron salts are very effective inhibitors. It has recently been reported that iron pentacarbonyl is an effective initiator for the reaction.²⁶⁴ The formation of additive dimers ($\text{R}_3\text{SiCH}_2\text{CHRCH}_2\text{SiR}_3$) is suggestive of the free radical character of the iron pentacarbonyl-initiated reaction.

Ultraviolet radiation is a generally effective and often very convenient initiator. Peroxides appear to give higher yields of adduct, but in the addition of trichlorosilane to 2-methyl-2-butene the higher yield is obtained with ultraviolet radiation.²⁵⁹ Triphenylsilane adds to 1-octene in the presence of benzoyl peroxide but not under ultraviolet irradiation.²⁶⁵ In the additions of trichlorosilane and of methyldichlorosilane to a number of fluorinated olefins, higher yields were obtained with di-*t*-butyl peroxide than with ultraviolet radiation,²⁶⁶ but Haszeldine and co-workers have obtained excellent yields in additions to fluorinated olefins by irradiation

²⁵⁹ Pietrusza, Sommer, and Whitmore, *J. Am. Chem. Soc.*, **70**, 484 (1948).

²⁶⁰ El-Abbady and Anderson, *J. Am. Chem. Soc.*, **80**, 1737 (1958).

²⁶¹ Lipscomb, U.S. pat. 2,570,462 [*C.A.*, **46**, 6141 (1952)].

²⁶² Ernster and Lipscomb, U.S. pat. 2,570,463 [*C.A.*, **46**, 6141 (1952)].

²⁶³ Speier and Webster, *J. Org. Chem.*, **21**, 1044 (1956).

²⁶⁴ Freidlina, Chukovskaya, and Ts'ao, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, **127**, 551 (1959).

²⁶⁵ Fuchs and Gilman, *J. Org. Chem.*, **22**, 1009 (1957).

²⁶⁶ McBee, Roberts, and Puerekhauer, *J. Am. Chem. Soc.*, **79**, 2329 (1957).

of the reactants in sealed quartz tubes²⁶⁷⁻²⁶⁹ Among the other initiators azo compounds appear to be about as effective as benzoyl peroxide,^{261,262} and γ -ray irradiation has been used to obtain high yields of adducts from a variety of olefins.²⁶⁰ Ozone has been claimed to be an initiator in the addition of silanes to perhalogenated olefins,²⁷⁰ and iron pentacarbonyl²⁶⁴ has been reported to promote additions of triethoxysilane, a compound with which peroxides and ultraviolet irradiation are quite ineffective.²⁵⁹

The purely thermal reaction is satisfactory if the olefin does not polymerize readily and if the reactants and products have adequate stability at the required temperature (160-400°). These reactions are usually carried out in autoclaves under pressure, but it is possible to use a flow system with a hot tube (400-600°).^{271,272} For the preparation of 1:1 adducts, the high-temperature reaction has two drawbacks. It favors telomerization with polymerizable olefins and β -halogen elimination with haloolefins (see discussion below).

The formation of higher telomers is frequently observed in silane additions to reactive olefins. With ethylene or propylene, telomer formation is unimportant in the peroxide- or azo-catalyzed reactions²⁷³ unless the reaction is performed under high pressure.²⁶¹ Good yields of telomers having up to about 6 olefin units are obtained, however, by thermal reaction at 250-350°.²⁷³ Trichlorosilane,^{274,275} methyldichlorosilane,^{273,276} phenyldichlorosilane,²⁷³ and triethylsilane²⁷³ have been telomerized with ethylene and with propylene under such conditions. Telomer formation is also observed in the ultraviolet-catalyzed additions of trichlorosilane and dimethylsilane to tetrafluoroethylene.^{267,277} With very readily polymerizable olefins such as acrylonitrile, methyl acrylate, and styrene, only telomers are obtained regardless of the initiator used.²⁷⁸ It is possible to control the extent of telomerization to a considerable degree by variation in reactant ratios. Thus, in the reaction between trichlorosilane and tetrafluoroethylene,²⁷⁷ an olefin-to-silane ratio of 1:4

²⁶⁷ Geyer and Haszeldine, *J. Chem. Soc.*, 1957, 1938.

²⁶⁸ Geyer and Haszeldine, *J. Chem. Soc.*, 1957, 3925.

²⁶⁹ Geyer, Haszeldine, Leedham, and Marklow, *J. Chem. Soc.*, 1957, 4472.

²⁷⁰ Farbenfabriken Bayer, Brit. pat. 764,288 [*C.A.*, 51, 14786 (1957)].

²⁷¹ White and Roehow, *J. Am. Chem. Soc.*, 76, 3897 (1954).

²⁷² Midland Silicones, Ltd., Brit. pat. 752,700 [*C.A.*, 51, 7403 (1957)].

²⁷³ Freidlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1957, 1353.

²⁷⁴ Nesmeyanov, Freidlina, and Chukovskaya, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, 113, 197 (1957).

²⁷⁵ Nesmeyanov, Freidlina, and Chukovskaya, *Tetrahedron*, 1, 248 (1957).

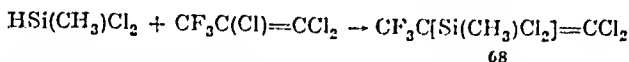
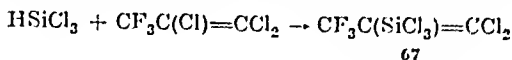
²⁷⁶ Nesmeyanov, Freidlina, and Chukovskaya, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, 112, 41 (1957).

²⁷⁷ Haszeldine and Marklow, *J. Chem. Soc.*, 1956, 962.

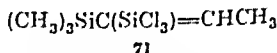
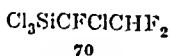
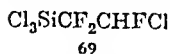
²⁷⁸ Speier, Zimmerman, and Webster, *J. Am. Chem. Soc.*, 78, 2278 (1956).

gave the 1:1 adduct in 60% yield, while a ratio of 5:6 gave only 35% of this adduct along with 65% of higher telomers.

The direction of addition of silyl radicals to olefins can usually be predicted from consideration of the relative stabilities of the alternative intermediate radicals as discussed in the introduction to this chapter. Thus, with terminal olefins, the addition is normally to the terminal carbon atom. Two apparent exceptions were reported for the additions of trichlorosilane and methyldichlorosilane to 1,1,2-trichloro-3,3,3-trifluoropropene.²⁶⁶ The products, 67 and 68, probably arise through initial attack of the silyl radicals on the central carbon atom followed by β elimination of a chlorine atom. The thermal addition of trichlorosilane



to chlorotrifluoroethylene is reported to yield both possible 1:1 adducts, 69 and 70.^{279,280} This is surprising in view of other radical additions to this olefin in which attack occurs exclusively on the CF_2 group. The photochemical reaction of trichlorosilane with chlorotrifluoroethylene yields only adduct 69.²⁸¹



Additions to monosubstituted acetylenes occur at the terminal carbon atom.^{282,283} The only disubstituted acetylene studied is trimethylsilylpropyne, which is reported to give the adduct 71 on peroxide-initiated addition of trichlorosilane.²⁸⁴ In a recent study Benkeser and co-workers have shown that peroxide-initiated additions of trichlorosilane to 1-pentyne, 1-hexyne, 1-heptyne, and 3-methyl-1-butyne proceed stereoselectively to produce approximately 3:1 mixtures of *cis*- and *trans*-olefins.^{283,285} The *trans*-olefin was the major product with 3,3-dimethyl-1-butyne.²⁸⁵

The additions of trichlorosilane to hexafluoro-1,3-butadiene at 200–250°^{279,280} and to 1,3-butadiene at 330°²⁵⁸ result in formation of the 1,2 rather than the 1,4 adducts.

A considerable number of compounds having one or more hydrogen

²⁷⁹ Midland Silicones, Ltd., Brit. pat. 746,510 [*C.A.*, 51, 7402 (1957)].

²⁸⁰ Haluska, U.S. pat. 2,800,494 [*C.A.*, 51, 17982 (1957)].

²⁸¹ Hazeldine and Young, *J. Chem. Soc.*, 1960, 4503.

²⁸² Burkhard, *J. Am. Chem. Soc.*, 72, 1402 (1950).

²⁸³ Benkeser and Hickner, *J. Am. Chem. Soc.*, 80, 5298 (1958).

²⁸⁴ Shehukovskaya, Petrov, and Egoroff, *J. Gen. Chem. USSR (Engl. Transl.)*, 26, 3713 (1956).

²⁸⁵ Benkeser, Burrous, Nelson, and Swisher, *J. Am. Chem. Soc.*, 83, 4385 (1961).

atoms attached to silicon undergo free radical additions to olefins. Silane itself adds to ethylene at 450–510° in a flow system to give a mixture consisting largely of ethyl- and diethylsilane together with disilanes, trisilanes, etc.²⁵¹ With ultraviolet irradiation (mercury photosensitization), the major reaction products are ethylsilane, *n*-butylsilane, and ethanedisilane.²⁷¹ Stepwise additions of silane can be effected thermally to give products of the type $RR'SiH_2$, since higher temperature is required for reaction of the second hydrogen atom.²⁵⁵ It has been concluded that, the higher the molecular weight of the olefin, the more readily it undergoes polysubstitution with silane. Thus isobutylene gives mainly tetra-isobutylsilane, even at 100°, while ethylene gives chiefly monoethylsilane up to about 200°.²⁵⁵

The presence of electronegative groups on silicon facilitates addition.²⁵⁹ Trichlorosilane reacts much faster than methylchlorosilane,^{257,267} whereas trialkylsilanes and trialkoxysilanes react very slowly, if at all.^{257,259} The reported reactivities of silanes seem to vary widely. For example, whereas triethoxysilane is unreactive toward 1-octene with peroxides or ultraviolet radiation²⁵⁹ and methyl-*n*-propylsilane gives almost no adduct with 1-pentene under similar conditions,²⁵⁷ methyl diethoxysilane is reported to give a 79% yield of adduct with *n*-heptafluoropropylethylene on ultraviolet irradiation for 3 days.²⁶⁹ In additions to cycloolefins, ultraviolet irradiation gives higher yields with tribromosilane than with trichlorosilane.^{268,269} Similarly, alkyl dibromosilanes appeared to be more reactive than alkyl dichlorosilanes with either ultraviolet or peroxide initiation.

Except for the presence of interfering functional groups such as hydroxyl or amino, there appear to be no limitations on the nature of the olefins to which silanes can be added. Silanes have been added to ethylene, tetrafluoroethylene, tetramethylethylene, methyl oleate, cyclohexene, β -pinene, acrolein diethyl acetal, and a host of other olefins. Not all silanes will add to every olefin, however. Triphenylsilane, which gives good yields of adducts with straight-chain alkenes, does not add to cyclohexene.^{290,291} Allyl chloride reacts with trichlorosilane to give the 1:1 adduct in 20% yield,²⁵⁹ but with phenylsilane complex products only are obtained.²⁷⁸ With readily polymerizable olefins, there is often a tendency to telomer formation, and this may be sufficient in certain

²⁵¹ Wolfe and Cook, U.S. pat. 2,786,862 [C.A., 51, 13904 (1957)]

²⁵⁷ Seyferth and Rochow, *J. Org. Chem.*, 20, 250 (1955)

²⁵⁹ Nametkin, Topchiev, and Charayakova, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, 111, 767 (1956)

²⁶⁹ Topchiev, Nametkin, and Solovova, *Doklady Akad. Nauk SSSR*, 86, 965 (1952) [C.A., 47, 10471 (1953)]

²⁹⁰ Gilman and Miles, *J. Am. Chem. Soc.*, 80, 811 (1958)

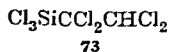
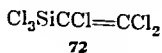
²⁹¹ Merten and Gilman, *J. Am. Chem. Soc.*, 76, 2798 (1954)

instances (e.g., styrene) to preclude the isolation of 1:1 adducts. Various statements can be found in the literature regarding the relationship of structure to reactivity. The following order of relative velocities of trichlorosilane addition (at 280°) to a series of substituted ethylenes suggests *no* strong steric influence: $\text{CH}_2=\text{CH}_2 < (\text{CH}_3)_2\text{C}=\text{CH}_2 < \text{CH}_3\text{CH}=\text{CH}_2 < \text{C}_2\text{H}_5\text{CH}=\text{CH}_2 < \text{CH}_3\text{CH}=\text{CHCH}_3 < (\text{CH}_3)_2\text{C}=\text{CHCH}_3 < (\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$.²⁹²

In additions to a series of olefins of the structure $\text{X}_3\text{SiCH}_2\text{CH}=\text{CH}_2$, electronegative groups on silicon ($\text{X} = \text{C}_6\text{H}_5$ or Cl) are reported to activate the double bond.²⁹³ Also, when X is an alkyl group, the activity of the double bond increases with increasing size of the substituent.

A surprising lack of reactivity has been noted with perfluoropropylene, which readily undergoes free radical additions of thiols, hydrogen bromide, etc., but gives only traces of adduct with trichlorosilane in the presence of peroxides or ultraviolet radiation.²⁹⁶ Prolonged heating at 180° gave no adduct,²⁹⁰ while at 200–300° a 14% yield of adduct was obtained.²⁷⁹ Other fluorinated olefins, including tetrafluoroethylene, 3,3,3-trifluoropropene, and 2,3,3,4,4,4-hexafluoro-1-butene are quite reactive and give adducts in high yield.^{266,269} No reaction occurs between phenylsilane and allyl cyanide or allylmercaptotrimethylsilane when *t*-butylperbenzoate is used as catalyst.²⁷⁸ Under the same conditions, allyl alcohol and allylamine give only complex products, presumably because of interaction of the $\text{Si}-\text{H}$ hydrogen atoms with the hydroxyl or amino groups. Protection of the hydroxyl group of allyl alcohol by a trimethylsilyl group permits the reaction to proceed normally.

Reaction of silanes with chloroethylenes frequently results in the formation of vinylsilanes rather than saturated 1:1 adducts.^{294–296} This is especially true at higher temperatures, although mixtures of the saturated adduct and the vinylsilane sometimes result from peroxide- or ultraviolet-initiated reactions at moderate temperatures.²⁹⁷ At 500–600°, the sole product of reaction between trichlorosilane and tetrachloroethylene is trichlorovinyltrichlorosilane (72), while at 125° with peroxide initiators the product is a mixture of 72 (12.6 parts) and 1,1,2,2-tetrachloroethyl trichlorosilane (73) (4.7 parts).²⁹⁷



²⁹² Voronkov, Romanova, and Smirnova, *Chem. Listy*, 52, 640 (1958) [*C.A.*, 52, 13615 (1958)].

²⁹³ Topchiev, Nametkin, Chernysheva, and Durgar'you, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, 110, 545 (1956).

²⁹⁴ Midland Silicones, Ltd., Brit. pat. 737,963 [*C.A.*, 50, 10760 (1956)].

²⁹⁵ Agre and Hilling, *J. Am. Chem. Soc.*, 74, 3895 (1952).

²⁹⁶ Mironov and Leites, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1959, 1957.

²⁹⁷ McBee, Roberts, and Puerckhauer, *J. Am. Chem. Soc.*, 79, 2326 (1957).

The formation of these unsaturated products occurs not as a result of dehydrohalogenation of the 1.1 adduct, but through β -elimination of a halogen atom from the intermediate radical.²⁹⁵ A method for preparing

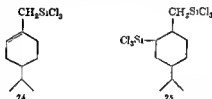


vinylsilanes consists in passing a mixture of the appropriate silane and vinyl chloride through a quartz tube at 550–600°.²⁷² In this way, vinyl-trichlorosilane was obtained in 53% yield from trichlorosilane and methyl-vinyldichlorosilane in 59% yield from methyldichlorosilane.

Another example of what is apparently a β -elimination occurs in the thermal reaction between trichlorosilane and 2,4,4-trimethyl-1-pentene.^{292,293}



The addition of trichlorosilane to β -pinene^{290–301} proceeds with carbon skeleton rearrangement in a manner entirely analogous to that observed in the addition of chloroform.³⁰² The resultant 1.1 adduct has the structure 74.³⁰² In the presence of a large excess of trichlorosilane and



under prolonged ultraviolet irradiation, a second molecule of the silane adds to give the adduct 75

Comparison with Other Methods

A number of different methods are available for the formation of silicon-carbon bonds. The most important are (1) the reaction of Grignard reagents or other organometallics with halosilanes or alkoxy-silanes, (2) the direct synthesis from silicon and alkyl or aryl halides, (3) the Wurtz-Fittig condensation of silicon halides with organic halides, and (4) the metal and metal salt-catalyzed additions of silanes to alkenes

²⁹² Plueddemann, U.S. pat. 2,642,447 [C.A., 43, 5206 (1954)].

²⁹³ Goldblatt and Oldroyd, U.S. pat. 2,533,240 [C.A., 45, 2262 (1951)].

²⁹⁴ Fraunfel, *Bull. Soc. Chim. France*, 1933, 292.

²⁹⁵ Fraunfel and Calas, *Compt. Rend.*, 240, 203 (1955).

³⁰² Calas and Fraunfel, *Compt. Rend.*, 243, 593 (1956).

³⁰³ du Pont, Dulou, and Clement, *Bull. Soc. Chim. France*, 1951, 257.

and alkynes. These and other methods are treated at some length by other authors.³⁰⁴

From the standpoint of its relationship to the work discussed above, the metal- and metal salt-catalyzed addition of silanes to unsaturates warrants some additional comment. The most commonly used metal and metal salt catalysts are platinum on charcoal or on γ -alumina, chloroplatinic acid, potassium chloroplatinate, or palladium. Ruthenium chloride, osmium tetroxide on carbon, and several other compounds of these elements have also been used. This method overlaps the free radical-catalyzed reaction to a considerable extent, and it frequently affords improved yields of product. This is especially true for additions to acetylenes.^{283,284} 1-Hexyne gives a 36% yield of adduct with trichlorosilane in the peroxide-initiated reaction, but a 93% yield with a platinum-on-charcoal catalyst. Phenylacetylene fails to give any adduct with peroxide but gives an 82% yield with the platinum-on-carbon catalyst.²⁸³ These catalysts permit the preparation of simple adducts from readily polymerizable olefins such as styrene or acrylonitrile, a feat either difficult or impossible under free radical conditions.³⁰⁵ Despite the considerable overlap between these two methods, there exist certain differences of important synthetic consequence:

(i) Whereas the free radical-catalyzed additions are almost never accompanied by rearrangement, this is not true for the ionic (metal- or salt-catalyzed) additions. The ionic additions of trichlorosilane and of methylchlorosilane to 3-heptene and 2-pentene give the *n*-heptyl and *n*-pentyl adducts exclusively.^{305,306}

(ii) Additions of silanes to acetylenes proceed stereoselectively to give the *trans*-olefin with free radical catalysts and the *cis*-olefin with ionic catalysts.^{283,285}

(iii) With butadiene, metal-catalyzed addition yields the 1,4 adduct,³⁰⁷ while the thermal (free radical) reaction gives the 1,2 adduct.²⁵⁸

The use of platinum catalysts with perhalogenated olefins is reported to result in explosions on occasion.³⁰⁸ Hence due caution should be observed with such systems.

A variety of other catalysts have been used with varying degrees of success for the addition of silanes to unsaturates. Among these should be mentioned amines such as triethylamine, pyridine, and piperidine.³⁰⁹

³⁰⁴ Eaborn, *Organosilicon Compounds*, Academic Press, Inc., New York, 1960.

³⁰⁵ Speier, Webster, and Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

³⁰⁶ Saarn and Speier, *J. Am. Chem. Soc.*, **80**, 4104 (1958).

³⁰⁷ Wagner, U.S. pat. 2,637,738 [*C.A.*, **48**, 8254 (1954)].

³⁰⁸ Tarrant, Dyckes, Dunmire, and Butler, *J. Am. Chem. Soc.*, **79**, 6536 (1957).

³⁰⁹ Nozakura, *Bull. Chem. Soc. Japan*, **29**, 322, 326, 784 (1956).

Experimental Conditions

The experimental conditions for effecting the free radical addition of silanes to olefins are usually simple and straightforward. The silane and olefin are mixed, the initiator (peroxide or azo) added, and the mixture heated or, alternatively, the mixture is irradiated with ultraviolet or ionizing radiation. Solvents are rarely used, excess of the silane generally serving this function. With olefins that are susceptible to telomerization a large excess of the silane is necessary to obtain good yields of the 1:1 adducts. It is sometimes advantageous to add a mixture of the olefin and initiator to the heated silane, especially if the silane contains more than one hydrogen atom and the monoadduct is desired.²⁷⁸ A favorable attribute of this system, as of free radical-initiated additions in general, is the simplicity of isolation of the product. Fractional distillation is usually all that is required.

ADDITION OF GERMANES TO OLEFINS

Additions of germanes to olefins are analogous to the additions of silanes. However, the germane reaction has been studied less extensively. The examples reported include additions of trichlorogermane, trialkylgermanes, and triphenylgermane to various olefins. The reaction is apparently free radical in nature, since telomers are sometimes formed,³¹⁰ and initiation by peroxides or ultraviolet light is frequently required.³¹⁰⁻³¹² Evidence has recently been presented that organotin hydrides, which in contrast to silanes and germanes had been considered to undergo solely ionic addition to olefins,^{313,314} do add by a free radical process.³¹⁵

Germanes are more reactive than the corresponding silanes in free radical additions. Thus, in the absence of initiators, temperatures in the range 160-400° are required to effect the addition of silanes to olefins,²³⁸ while trichlorogermane adds exothermally to various olefins at room temperature,³¹⁵ and trialkylgermanes add to acrylonitrile and to acrylate esters at the reflux temperature. The difference in reactivity is illustrated further by the observation that triphenylgermane adds to triphenylallylgermane in 85% yield under peroxide initiation, whereas triphenylsilane fails to add under similar conditions.³¹¹

³¹⁰ Leebre and Satgé, *Compt. Rend.*, **247**, 471 (1958).

³¹¹ Gilman and Gerow, *J. Am. Chem. Soc.*, **79**, 362 (1958).

³¹² Meen and Gilman, *J. Org. Chem.*, **22**, 694 (1957).

³¹³ Van der Kerk, Luyten, and Noltes, *Chem. & Ind. (London)*, 1956, 352.

³¹⁴ Fuchs and Gilman, *J. Org. Chem.*, **22**, 1008 (1957).

³¹⁵ Petrov, Mironov, and Dzharinskaya, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)* **123**, 739 (1959).

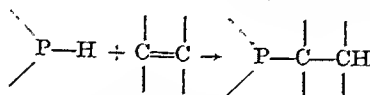
Triphenylgermane fails to add to 1,1-diphenylethylene with peroxide or ultraviolet initiation, and in its reaction with cyclohexene some tetraphenylgermane³¹⁴ is formed in addition to the 1:1 adduct.

The experimental conditions for reaction of germanes with olefins can be inferred from those of the silanes, bearing in mind the generally greater reactivity of the germanes.

RADICAL ADDITIONS TO FORM PHOSPHORUS-CARBON BONDS*

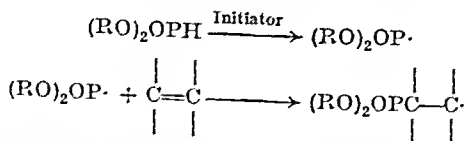
Compounds Containing P—H Bonds

The free radical addition to olefins of a variety of phosphorus compounds containing P—H bonds is a general reaction. Examples involving phosphine,³¹⁶⁻³¹⁸ substituted phosphines,^{318,319} phosphorous acid



[HP(O)(OH)₂]^{320,321} and esters,³²²⁻³²⁵ hypophosphorous acid [H₂P(O)OH]³²⁵ and salts,^{327,328} and phosphinic acid derivatives [RPH(O)OR]³²⁷ have been reported. Although no extensive studies of mechanism have been made, it seems certain that the reactions occur by a radical chain mechanism, written here for addition of a dialkyl phosphite.^{317,324}

In this scheme, the (RO)₂OP· radical is the adding species, and, in the



* Phosphorus addition reactions, ionic and radical, have been reviewed by Crofts.³²⁹ Radical additions have been discussed by Walling (ref. 45, p. 341).

³¹⁶ N. V. deBataaf. *Pet. Maats., Brit. pat.* 673,451 [*C.A.*, 47, 5426 (1953)].

³¹⁷ Stiles, Rust, and Vaughan, *J. Am. Chem. Soc.*, 74, 3282 (1952).

³¹⁸ Rauhut, Currier, Semsel, and Wyatrach, *J. Org. Chem.*, 26, 5138 (1961).

³¹⁹ Arbuzov, Vinokurova and Perfil'eva, *Proc. Acad. Sci. USSR, Chem. Sect. (Engl. Transl.)*, 127, 657 (1959).

³²⁰ Griffin, *J. Org. Chem.*, 25, 665 (1960).

³²¹ Griffin and Wells, *J. Org. Chem.*, 24, 2049 (1959).

³²² Barnes and David, *J. Org. Chem.*, 25, 1191 (1960).

³²³ Kharasch, Mosher, and Bengelsdorf, *J. Org. Chem.*, 25, 1009 (1960).

³²⁴ Stiles, Vaughan, and Rust, *J. Am. Chem. Soc.*, 80, 714 (1958).

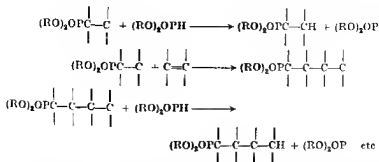
³²⁵ Bittles and Joyce, U.S. pat. 2,559,754 [*C.A.*, 46, 1926 (1952)].

³²⁶ Williams and Hamilton, *J. Am. Chem. Soc.*, 77, 3411 (1955).

³²⁷ Stiles and Rust, U.S. pat. 2,724,718 [*C.A.*, 50, 10124 (1956)].

³²⁸ N. V. deBataaf. *Pet. Maats., Brit. pat.* 669,918 [*C.A.*, 46, 8145 (1952)].

³²⁹ Crofts, *Quart. Rev. (London)*, 12, 341 (1955).

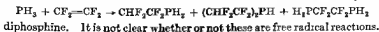


products whose structures have been determined, the phosphorus atom is found on the carbon atom ordinarily attacked by radicals. Reversibility in the addition step has been demonstrated in the additions of phenylphosphine, 2-cyanoethylphosphine, and di-*n*-butylphosphine to *cis*-2-butene.³²⁰ Other aspects of the mechanism and stereochemistry have not been investigated.

Reactions of phosphine and substituted phosphines with olefins have been initiated by ultraviolet radiation, x-radiation, peroxides, and azo catalysts. Additions of phosphine have been carried out with terminal, internal, and cyclic olefins. With terminal olefins, all the P—H bonds can participate. Thus from 1-octene, octyl (0–75%), dioctyl (0–39%), and trioctyl (4–100%) phosphine are formed, the relative yields depending on the ratio of starting materials.³¹⁶



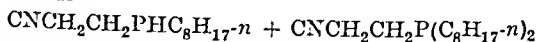
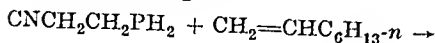
With isobutylene and cyclohexene, steric problems arise in the addition of the third molecule of olefin, so that triisobutylphosphine is formed in low yield and tricyclohexylphosphine not at all, even though good yields of the mono- and di-adducts are formed. With easily polymerizable olefins, e.g., styrene and ethyl acrylate, conversions in good yield to the mono-, di-, and tri-adducts are accompanied by relatively small amounts of telomerization. This indicates that chain transfer on the P—H bonds of phosphines occurs readily. The major product from the ultraviolet-initiated reaction with allyl chloride is a hard insoluble phosphorus-containing polymer.³¹⁷ Phosphine has been added to several fluoroolefins at 150° without added catalysts.³²¹ From tetrafluoroethylene a mono- and a di-adduct are obtained in addition to tetrafluoroethylene



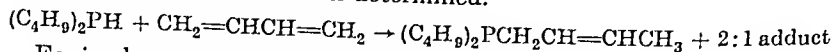
³²⁰ Pellon, *J. Am. Chem. Soc.*, **83**, 1915 (1961).

³²¹ Parshall, England, and Lindsey, *J. Am. Chem. Soc.*, **81**, 4801 (1959).

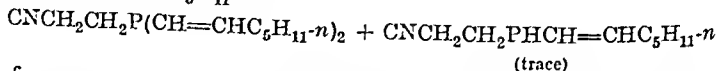
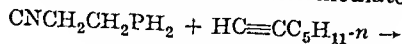
Mono- and di-substituted phosphines have been used to prepare unsymmetrical secondary and tertiary phosphines;³¹⁸ for example, 2-cyanoethylphosphine and 1-octene form monoöetyl- and dioetyl-2-cyanoethylphosphine.



Dibutylphosphine reacts with butadiene via 1,4 addition to form dibutyl-2-*trans*-butenylphosphine and a small amount of a 2:1 adduct whose structure has not been determined.

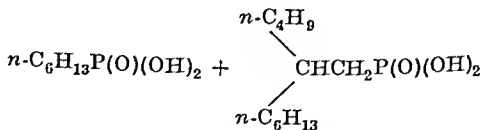
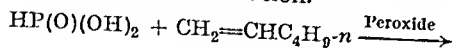


Equimolar amounts of 2-cyanoethylphosphine and 1-heptyne form 2-cyanoethyl-bis-(1-heptenyl)phosphine in a 26% yield accompanied by only a trace of the intermediate monoadduct.³¹⁸ Bis-(2-cyanoethyl)-

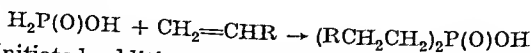


phosphine forms a monoadduct with 1-heptyne. In neither of these cases are products found which result from further addition of phosphine to the unsaturated adducts.

The ultraviolet- or peroxide-initiated additions of phosphorous acid have given yields of 18–28% of 1:1 adducts (phosphonic acids), the major products being higher telomers or polymers of the olefin.^{320,321} In several cases, e.g., 1-octene, 1-hexene, and 1-decene, the 2:1 adducts have been isolated and have been shown to be those resulting from a conventional head-to-tail telomerization.³²⁰



The peroxide-initiated additions of aqueous hypophosphorous acid to terminal olefins have been used to prepare dialkylphosphinic acids in yields up to 40%.³²⁶ No 1:1 adducts were reported. Analogous additions of sodium hypophosphite have been reported to give high yields of 1:1 adducts.^{327,328,332}



Peroxide-initiated additions of a phosphinic ester, $\text{C}_6\text{H}_5\text{PH}(\text{O})\text{OC}_2\text{H}_5$, and the sodium salt of a phosphinic acid, $n\text{-C}_6\text{H}_{13}\text{PH}(\text{O})\text{ONa}$, to terminal olefins gave the expected 1:1 adducts.^{327,328}

³³² Smith, U.S. pat. 2,648,695 [*C.A.*, 48, 8252 (1954)].

Of all the additions of compounds containing P—H bonds, those involving dialkyl phosphites to give dialkylphosphonates have received the most attention. They have been initiated with peroxides, azonitriles, and ultraviolet radiation. The ratio of reactants affects both the rate of



the reaction and the composition of the product.³²⁴ A high concentration of the dialkyl phosphite results in a long kinetic chain and a predominance of the 1:1 adduct, while a high concentration of the olefin shortens the chain length and results in greater proportions of higher telomers.³²⁵ The effect of high olefin concentration on the rate indicates that the olefin is actually an inhibitor of the addition reaction. The mechanism for this inhibition no doubt involves abstraction of allylic hydrogen by the intermediate radical resulting in the formation of a stable allylic radical, thus effectively interrupting the kinetic chain. Both effects of high olefin concentration, i.e., telomerization and hydrogen abstraction, are attributable to relatively low chain transfer constants for dialkyl phosphites.³²⁴ Similar arguments have been applied to correlate the results in phosphorous acid additions.^{320,323}

Both terminal and internal olefins readily undergo radical addition of dialkyl phosphites.³²⁴ Ethylene and tetrafluoroethylene yield telomers with dialkyl phosphites, the length of the carbon chain depending on the olefin pressure employed.^{325,335,336} Additions to terminal olefins form 1:1 adducts with the phosphorus atom attached to the terminal carbon. The additions of diethyl phosphite to 2-hexene and 2-heptene are reported to proceed at a lower rate than the corresponding additions to terminal olefins, and to yield a single 1:1 adduct with phosphorus in the 2 position in each case.³³⁷

In the one example of the addition of a dialkyl phosphite to an α,β -unsaturated ester reported, both 1:1 adducts were found.^{327,328} This result is surprising, since in other radical additions to α,β -unsaturated



³²⁴ Preis, Myers, and Jensen, *J. Am. Chem. Soc.*, **77**, 6225 (1955).

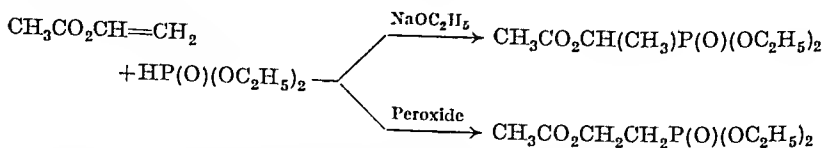
³²⁵ Sasun, Olezewski, Russell, and Swern, *J. Am. Chem. Soc.*, **81**, 4275 (1959).

³²⁶ Hanford and Joyce, U.S. pat. 2,478,390 [C.A., **44**, 1126 (1950)].

³²⁷ Bruce, *J. Org. Chem.*, **26**, 3197 (1961).

³²⁸ Pudovik and Konovalova, *J. Gen. Chem., USSR (Engl. Transl.)*, **29**, 3305 (1959).

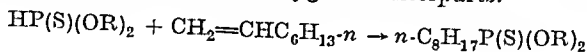
esters (e.g., the addition of phosphine to methyl acrylate) only β -substituted esters have been reported. Base-catalyzed additions of compounds containing P—H bonds to α,β -unsaturated carbonyl compounds and nitriles have been studied extensively,³²⁹ but apparently no comparative study of the two methods has been made. Both a base-catalyzed and a free radical addition of diethyl phosphite to vinyl acetate have been realized.³³⁸



Attempts to add dialkyl phosphites to unactivated double bonds thermally or with acid and base catalysts have been unsuccessful.³³⁷ Similarly, the addition of phosphorous acid to terminal olefins did not occur thermally or under acid catalysis.³²¹ It thus appears that, in contrast to additions of thiols, it is not possible to add compounds containing P—H bonds to unactivated olefins except by a radical procedure.

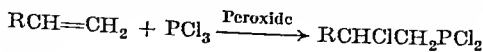
There have been no studies of additions of dialkyl phosphites to acetylenes.

A few ultraviolet- and peroxide-initiated additions of esters of thiophosphorous acid have been reported.³³⁹ These esters are apparently more reactive in additions than their oxygen counterparts.

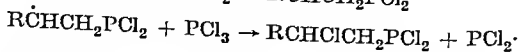
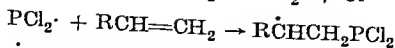
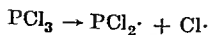


Other Phosphorus Compounds

A peroxide-initiated addition of phosphorus trichloride to olefins giving 1:1 adducts and higher-boiling materials of undetermined nature was reported in 1945 by Kharasch, Jensen, and Urry.³⁴⁰ A typical free radical chain mechanism in which the dichlorophosphine radical is the adding



species was proposed.



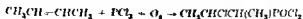
There has apparently been no further study of this reaction.

³³⁸ McConnell and Coover, *J. Am. Chem. Soc.*, **79**, 1961 (1957).

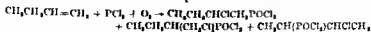
³³⁹ Pudovik and Konovalova, *J. Gen. Chem. USSR (Engl. Transl.)*, **30**, 2328 (1960).

³⁴⁰ Kharasch, Jensen, and Urry, *J. Am. Chem. Soc.*, **67**, 1864 (1945).

Somewhat related to the foregoing reaction is the oxidative chlorophosphonation of olefins by oxygen and phosphorus trichloride^{341,342} From 2-butene, 2-chlorobutyl-3 phosphonic dichloride was obtained, presumably by the radical addition of the elements of Cl and POCl₂. With 1-butene both 1,1 adducts were formed in addition to 2-chlorobutyl-3-



phosphonic dichloride. The last product could arise from a radical



substitution by the POCl₂ radical at the allylic position followed by ionic addition of hydrogen chloride. Further work is needed to define the mechanism of this reaction. An attempt to achieve the addition of diethyl phosphorochloridate, (C₂H₅O)₂P(O)Cl to 1-octene by a free radical procedure was unsuccessful.³²³ The additions of phosphorus pentachloride to olefins are presumably ionic reactions.

Free radical-induced reactions of alkyl and aryl dihalophosphines with olefins and dienes result largely in the formation of copolymers, in some cases (especially with dienes) approaching a 1:1 composition.³⁴³⁻³⁴⁶ Isoprene and phenyldichlorophosphine furnish a 1:1 copolymer in 45% yield. This reaction does not involve scission of P—Cl bonds followed by



addition to the olefin, but rather is apparently analogous to the radical copolymerization of sulfur dioxide with olefins.

White phosphorus reacts with oxygen and olefins in benzene solution by a radical chain process to form products with the approximate composition (olefin · P₂O₄).³⁴⁷ On the basis of hydrolysis studies these materials have been assigned a polymeric anhydride structure in which one phosphorus atom is bound to carbon in a phosphonic anhydride function and the other is linked to carbon through oxygen and is in the phosphite oxidation

³⁴¹ Zinov'ev and Soborovskii, *J. Gen. Chem. USSR, (Engl. Transl.)*, 29, 611 (1959).

³⁴² Soborovskii, Zinov'ev, and Muler, *Doklady Akad. Nauk SSSR*, 109, 98 (1956) [*C. A.*, 51, 1825 (1957)].

³⁴³ McCormack, U.S. pat. 2,671,077 [*C. A.*, 49, 6737 (1954)].

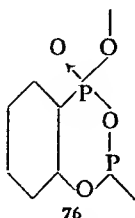
³⁴⁴ McCormack, U.S. pat. 2,671,079 [*C. A.*, 49, 6738 (1954)].

³⁴⁵ McCormack, U.S. pat. 2,671,078 [*C. A.*, 49, 6739 (1954)].

³⁴⁶ McCormack, *Reactions of Dienes with Phosphorus Compounds*, Gordon Research Conference, 1957.

³⁴⁷ Walling, Stacey, Jamison, and Haysen, *J. Am. Chem. Soc.*, 80, 4543, 4546 (1958).

level; for example, structure 76 has been proposed for the product from cyclohexene. The reaction is apparently general and the yields high



(70–100%). With 1-octene and olefins of higher molecular weight, further oxidation leads to products approaching the composition (olefin $\cdot P_2O_5$).

Experimental Conditions

The usual free radical initiators, e.g., peroxides, azonitriles, and ultraviolet radiation, are effective. In order to attain maximum yields of 1:1 adducts, a 1.5-fold or larger excess of the phosphorus compound is desirable. The peroxide-initiated reactions of dialkyl phosphites³³⁸ and phosphonates³²² have generally been carried out without solvents in sealed Pyrex tubes or metal autoclaves at the decomposition temperatures of the initiators. Open vessels can be used with high-boiling reactants.³²⁴ In ultraviolet experiments, temperatures ranging from room temperature to 100° have been used.³³⁷ In ultraviolet-initiated reactions with phosphine, the reactants are manipulated in a vacuum train, sealed in tubes, and irradiated at approximately room temperature.³¹⁷ Peroxide- and azonitrile-initiated additions of phosphine have been done in heptane solution in stainless steel autoclaves.³¹⁸ The peroxide-initiated additions of phosphorous³²¹ and hypophosphorous acids³²⁶ have been carried out in aqueous solution.

RADICAL ADDITIONS TO FORM CARBON-NITROGEN BONDS

The most important additions to olefins of radicals bearing the odd electron on nitrogen are the additions of dinitrogen tetroxide and nitril chloride. Possibly the reactions of dinitrogen trioxide with olefins are homolytic,³⁴⁸ but the present evidence suggests that dinitrogen pentoxide reacts ionically,³⁴⁹ as does nitrosyl chloride generally. A recent paper indicates, however, that the addition of nitrosyl chloride to fluorinated

³⁴⁸ Shechter and Ley, *Chem. & Ind. (London)*, 1955, 535.

³⁴⁹ Stevens and Emmons, *J. Am. Chem. Soc.*, **79**, 6008 (1957).

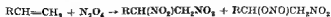
olefins is a free radical process.³⁵² Very few additions of amino radicals to olefinic double bonds have been reported.³⁵¹

The reaction of dinitrogen tetroxide with olefins and acetylenes has been studied for many years, but it was not until the studies of Levy, Scaife, and co-workers³⁵²⁻³⁵⁴ in the 1940's that control of the reaction to give isolable products in good yield was accomplished. The earlier work generally resulted in the formation of unstable solids or oils from which the isolation of pure compounds was difficult or impossible. The reports of this early work are often conflicting, confused by questions of the nature and purity of the nitrogen oxides used and by lack of consistent nomenclature. Also, because of the unstable nature of many of the products, the analyses are frequently open to question and hence many of the interpretations and conclusions must be considered questionable. Riebsomer³⁵⁵ has reviewed the reactions of dinitrogen tetroxide up to 1945. In view of the existence of this review and the points noted regarding the older literature on this subject, the discussion and tabulation which follow deal only with work appearing since 1945.

By contrast, practically all the studies of the additions of nitril chloride are recent, and the customary attempt at complete coverage has been made. Discussion of the related dinitrogen tetroxide-halogen systems is included with that of nitril chloride.

Dinitrogen Tetroxide

Mechanism. The studies of Levy and co-workers³⁵²⁻³⁵⁴ showed that under properly controlled conditions the only products resulting from reaction of dinitrogen tetroxide with olefins are the vicinal dinitroalkane and nitro-nitrite, and that with unsymmetrical olefins the nitro group in the nitro-nitrite is always found on the carbon atom bearing the greater number of hydrogen atoms. In practice the products isolated are the dinitroalkane, the nitroalcohol, and some nitro-nitrate. The latter two products arise from hydrolysis and oxidation, respectively, of the nitro-nitrite. These observations were rationalized by the assumption of a



heterolytic cleavage of the tetroxide to $\text{NO}_2^+\text{NO}_2^-$ and subsequent addition. More recent studies of the reaction, however, support a free radical

³⁵⁰ Park, Stefani, and Lacher, *J. Org. Chem.*, **26**, 4017 (1961).

³⁵¹ Albizzati et al., *J. Am. Chem. Soc.*, **81**, 1489 (1959).

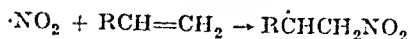
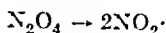
³⁵² Levy and Scaife, *J. Chem. Soc.*, **1946**, 1093, 1096, 1100.

³⁵³ Levy, Scaife, and Wilder Smith, *J. Chem. Soc.*, **1948**, 52.

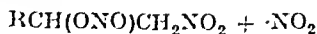
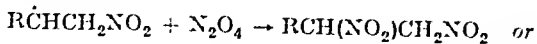
³⁵⁴ Levy and Rose, *Quart. Rev. (London)*, **1**, 358 (1948).

³⁵⁵ Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

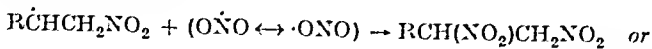
mechanism initiated by a homolytic dissociation of the dinitrogen tetroxide.



Chain process:



Non-chain process:



There is at present no evidence permitting a decision between the chain and non-chain processes. The principal evidence for the free radical nature of the addition can be summarized as follows: (1) The orientation in addition to unsymmetrical olefins is always specific and is not altered by the electronic character of substituents on the unsaturate.³⁵⁵ (2) In the addition of dinitrogen tetroxide to methyl acrylate, there is formed, along with the expected dinitro adduct and nitro-nitrite, an appreciable amount of nitrogen-containing polymer. (3) In the presence of such well-known chain transfer agents as bromotrichloromethane,^{357,358} bromoform,³⁵⁹ or iodine,³⁶⁰ formation of the normal adducts is suppressed, and the products obtained are those expected from interaction of a β -nitroalkyl radical with the transfer agent.

The addition of dinitrogen tetroxide exhibits stereoselectivity with a number of olefins. Cyclohexene and cyclopentene give both *cis*- and *trans*-nitro-nitrite adducts, the *trans* isomers predominating (58% and 84%, respectively). 1-Methylcyclohexene yields *trans*-1-methyl-2-nitrocyclohexyl nitrite exclusively.³⁵⁸ Similarly 9,10-octalin gives only *trans*-9,10-dinitrodcealin, and the major attack on norbornylene occurs in an *exo-cis* direction.³⁶¹ (See equation on p. 227.)

The most thoroughly investigated olefin from a stereochemical viewpoint is stilbene. *cis*-Stilbene is converted to *trans*-stilbene under the reaction conditions used. Addition to *trans*-stilbene gives mixtures of *meso*- and *dl*-dinitrodiphenylethane in a 2:3 ratio, and of *erythro*- and

³⁵⁵ Shechter and Conrad, *J. Am. Chem. Soc.*, **75**, 5610 (1953).

³⁵⁷ Brand and Stevens, *Chem. & Ind. (London)*, 1956, 469.

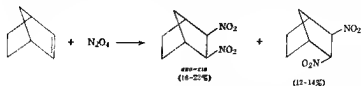
³⁵⁸ Brand and Stevens, *J. Chem. Soc.*, 1958, 629.

³⁵⁹ Baryshnikova and Titov, *Doklady Akad. Nauk SSSR*, **91**, 1099 (1953) [*C.A.*, **48**, 10629 (1954)].

³⁶⁰ Stevens and Emmons, *J. Am. Chem. Soc.*, **80**, 338 (1958).

³⁶¹ J. J. Gardikes, Doctoral Dissertation, Ohio State University, 1960; *Dissertation Abstr.*, **21**, 757 (1960).

threo-1-hydroxy-2-nitro-1,2-diphenylethano (from the nitro-nitrite after hydrolysis) in about a 1:2 ratio, when the reaction is carried out in ether



in the absence of oxygen.^{362,363} Thus the major isomers are those deriving from *cis* rather than *trans* addition, and it has been suggested that these major isomers are formed more rapidly because the structure of the transition state for reaction of the 2-nitro-1,2-diphenyl-1-ethyl radical with the nitrating agent (N_2O_4 or NO_2), resembles the reactants and attack occurs at the greatest rate from the more accessible (i.e., *cis*) direction.³⁶²

Scope and Limitations. There are no apparent restrictions on the nature of the olefin which can react with dinitrogen tetroxide to give dinitro adducts and nitro nitrites. Additions to terminal and internal acyclic olefins, polyhaloethylenes, cyclic olefins, conjugated olefins (e.g., styrene and butadiene), and α,β -unsaturated esters, among others, have been recorded. In reaction with fluoroethylenes, only the dinitro adducts have been reported.^{364,365} Under forcing conditions, it has been possible to form tetranitroalkanes by the addition of dinitrogen tetroxide to 2,3-dinitro-2-butene and 3,4-dinitro-3-hexene.³⁶⁶ While additions to disubstituted acetylenes proceed readily, additions to terminal acetylenes are not useful because of the unstable nature of the reaction mixtures.³⁶⁷⁻³⁶⁹

The use of oxygen as a carrier gas for the dinitrogen tetroxide affects the course of the reaction in various ways, according to the olefin being nitrated. With simple terminal alkenes, oxygen prevents reduction of dinitrogen tetroxide to dinitrogen trioxide,^{352,354} and thereby permits a cleaner product mixture to be obtained. The only other apparent effect of the oxygen is to increase the amount of nitro-nitrate at the expense of

³⁶² Gardikes, Pagano, and Shechter, *J. Am. Chem. Soc.*, **81**, 5420 (1959), *Chem. & Ind. (London)*, 1958, 622.

³⁶³ Stevens, *J. Am. Chem. Soc.*, **81**, 3593 (1959).

³⁶⁴ Coffman, Raasch, Rigby, Barriek, and Hanford, *J. Org. Chem.*, **14**, 747 (1949).

³⁶⁵ Hazeldine, *J. Chem. Soc.*, 1953, 2075.

³⁶⁶ Grabel, Bugrovs, and Clapp, *J. Am. Chem. Soc.*, **77**, 1293 (1955).

³⁶⁷ Campbell, Shavel, and Campbell, *J. Am. Chem. Soc.*, **75**, 2400 (1953).

³⁶⁸ Schlubach and Rott, *Ann.*, **594**, 58 (1955).

³⁶⁹ Freeman and Erdmann, *J. Am. Chem. Soc.*, **79**, 1712 (1957).

nitro-nitrite. However, with a number of other olefins including camphene,³⁷⁰ allylbenzene,³⁷¹ stilbene,³⁶³ and styrene,³⁵⁹ the use of tetroxide and oxygen mixtures results in the formation of products different from those obtained in the absence of oxygen. Stilbene reacts with dinitrogen tetroxide in ether, in the *absence* of oxygen to give, after hydrolysis, a mixture of 1,2-dinitro-1,2-diphenylethane (53%) and 1-hydroxy-2-nitro-1,2-diphenylethane (23%). In the *presence* of oxygen, no dinitro adduct is found, but there are obtained a 25% yield of 1-nitro-2-nitrato-1,2-diphenylethane and a 24% yield of α -nitro- α -phenylacetophenone along with about 30% of 1-hydroxy-2-nitro-1,2-diphenylethane.³⁶³ Similar results are observed with the other olefins mentioned. It has been suggested that the effect of the oxygen in these instances may be due to its reaction with the relatively stable intermediate nitroalkyl radicals to give α -nitroperoxy radicals or α -nitroperoxynitrates.^{359,363}

The addition of dinitrogen tetroxide to diethyl maleate, with or without solvent, is reported to give both the bis-nitrite and the nitro-nitrite.³⁷² The formation of the bis-nitrite was inferred from the isolation of tartaric acid on hydrolysis. This is the only report of the formation of a bis-nitrite.

Undecylenic acid is claimed to give the 10-nitro-11-nitrito adduct instead of the expected 11-nitro-10-nitrito compound.³⁷³ This appears to warrant further investigation.

Experimental Conditions. The conditions worked out by Levy and co-workers³⁵²⁻³⁵⁴ for the reaction of olefins with dinitrogen tetroxide and the isolation of the products involve the use of pure tetroxide, conversion of the unstable nitro-nitrite to the stable nitro alcohol prior to isolation, and the use of ether or ester-type solvents which reduce the oxidizing activity of the dinitrogen tetroxide. These conditions, which overcame many of the difficulties encountered by earlier workers, have been widely adopted. Maintaining the temperature below about 25° is usually essential, and interference by dinitrogen trioxide (easily formed from dinitrogen tetroxide) can be prevented by adding a small amount of oxygen along with the dinitrogen tetroxide.

In general, the olefins are added slowly to pure dry dinitrogen tetroxide or preferably to a concentrated solution of dinitrogen tetroxide in ether or ester-type solvents at -10° to +25°. Under these conditions, addition of tetroxide to the double bond occurs to give only the dinitroalkane and

³⁷⁰ Stevens, *Chem. & Ind. (London)*, 1957, 1546.

³⁷¹ Stevens, *Chem. & Ind. (London)*, 1960, 499.

³⁷² Vasil'ev and Mikerin, *Sb. Statei Obsch. Khim., Akad. Nauk SSSR*, 1, 305 (1953) [*C.A.*, 49, 867 (1955)].

³⁷³ Vasil'ev, *J. Gen. Chem. USSR (Engl. Transl.)*, 26, 819 (1956).

the nitro-nitrite. Some oxidation of the latter to nitro-nitrate occurs in the presence of oxygen. It is essential to convert the very unstable nitro-nitrite to a nitro alcohol by treatment with cold water or methanol, before attempting the isolation of the products. Failure to do so almost invariably results in violent decomposition of the reaction mixture when the solvent is removed.

The choice of solvent is rather critical. The best solvents are ethers, such as dioxane, diethyl ether, methylal, tetrahydrofuran, and tetrahydropyran, or acetate esters, all of which form molecular addition compounds with dinitrogen tetroxide. Substituted ethers, with reduced electron availability at the oxygen atom (e.g., 2,2'-dichlorodiethyl ether), do not form molecular complexes with dinitrogen tetroxide³⁷⁴ and are found to be ineffective as solvents for its reaction with olefins³⁵⁴. The same thing can be said for hydrocarbons and chlorinated alkanes, although the latter have been used in the reaction of olefins with dinitrogen tetroxide/halogen mixtures³⁷⁵. While low temperatures and the use of an appropriate solvent are the normal conditions for successful reaction with most olefins, far more vigorous conditions are used with polyhalogenated olefins. Thus, in the formation of the dinitro adducts from chlorotrifluoroethylene, dichlorodifluoroethylene, and tetrafluoroethylene, mixtures of the olefin and pure dinitrogen tetroxide were heated in sealed vessels for several hours at 65°³⁶⁵.

The importance of using peroxide-free olefins has been stressed by Levy for the addition to cyclohexene.³⁷⁶ The order of mixing the reagents affects the relative proportions of the products to some extent. Slow addition of cyclohexene to an excess of tetroxide in ether gave 42% dinitrocyclohexane, 25% nitrocyclohexanol, and 18% nitrocyclohexyl nitrate, while addition of tetroxide slowly to a cyclohexene-ether solution gave the same products in amounts of 30%, 54%, and 2%, respectively.

Nitryl Chloride and Dinitrogen Tetroxide-Halogen Mixtures

Mechanism. The postulation of a free-radical chain mechanism for the addition of nitryl chloride to olefins³⁷⁷ receives support from the following observations. (1) The orientation of addition is the same to both electronegatively and electropositively substituted olefins. Terminal addition of a nitro group is observed with vinyl bromide (to give 1-bromo-1-chloro-2-nitroethane), with propylene and other terminal olefins, and with acrylonitrile, methyl acrylate, and acrylic

³⁷⁴ Rubin, Sessler, and Shechter, *J. Am. Chem. Soc.*, **74**, 877 (1952).

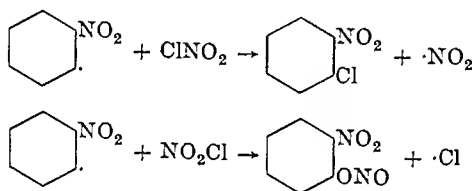
³⁷⁵ Bachman, Logan, Hill, and Standish, *J. Org. Chem.*, **25**, 1312 (1960).

³⁷⁶ Baldock, Levy, and Seale, *J. Chem. Soc.*, **1949**, 2627.

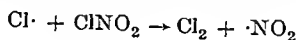
³⁷⁷ Shechter, Conrad, Daulton, and Kaplan, *J. Am. Chem. Soc.*, **74**, 3052 (1952).

acid. (2) In reaction with methyl acrylate, a 2:1 telomer, of structure $O_2NCH_2CH(CO_2CH_3)CH_2CHClCO_2CH_3$, has been isolated along with the 1:1 adduct.³⁷⁷ (3) The products obtained in the reaction of nitryl chloride with cyclohexene are most readily explained by a free radical mechanism.³⁵⁸

The principal products from the nitryl chloride-cyclohexene reaction are 1-chloro-2-nitrocyclohexane and *trans*-1,2-dichlorocyclohexane, together with 2-chlorocyclohexanol and 2-chlorocyclohexyl nitrate (both deriving from 2-chlorocyclohexyl nitrite), and 2-nitrocyclohexanol (deriving from 2-nitrocyclohexyl nitrite). These products are in agreement with a mechanism wherein initiation occurs mainly by addition of $\cdot NO_2$ to the double bond followed by transfer with nitryl chloride in either of two ways.



The formation of 2-chlorocyclohexyl nitrite indicates that some initiation must occur by chlorine atom addition, followed by transfer on nitryl chloride because initial attack by $\cdot NO_2$ always involves formation of a carbon-to-nitrogen rather than a carbon-to-oxygen bond. The formation of dichlorocyclohexane could be due to initiation by chlorine atom attack with subsequent transfer. However, the dichloro compound might also be formed by normal heterolytic addition of molecular chlorine which could arise by reaction of chlorine atoms with nitryl chloride. This process is



known to be important in the high-temperature decomposition of nitryl chloride.

It has recently been suggested that, whereas nitryl chloride adds by a free radical mechanism to double bonds with electron-withdrawing substituents, it may add ionically as $NO_2^+Cl^-$ to double bonds with electron-supplying groups.³⁷⁵ However, such an assumption does not appear to be required in order to explain all the presently known cases of addition.

Closely related to nitryl chloride additions are the reactions of olefins with dinitrogen tetroxide/halogen mixtures. The isolation of β -iodo-nitroalkanes in high yield as products of the reaction of dinitrogen tetroxide

with olefins in the presence of iodine has been used as evidence for the free radical nature of the dinitrogen tetroxide/olefin reaction³⁶⁰ However, recent studies have shown that, whereas haloethylenes and other olefins containing electronegative substituents react with N_2O_4/X_2 mixtures ($X_2 = Br_2$ or I_2) to give β -halonitroalkanes, other olefins such as ethylene, propylene, and 1-butene, under identical reactions conditions, gave only 1-haloalkyl-2-nitrates^{375,378} The latter products are undoubtedly formed by an ionic reaction It thus appears that N_2O_4/X_2 mixtures can react with simple non-electronegatively substituted olefins, to give either β -halonitro compounds or 1-haloalkyl-2-nitrates by what are probably competing free radical and ionic reactions and that the product formed is determined by the conditions chosen for the reaction (see "Experimental Conditions," p 232) Of interest, also, is the fact that in the vapor phase at 260–275° the reaction of propylene or of 1-butene with N_2O_4/Cl_2 gives rise to the 1-chloro-2-nitroalkanes along with major amounts of dichloroalkanes. This reaction no doubt is initiated by addition of a chlorine atom. In the liquid phase, only dichloroalkanes are formed

Scope and Limitations. The addition of nitryl chloride to olefins is apparently general, and no limitations with respect to the nature of the olefin have been noted. There is, however, considerable variation in reactivity of olefins with this reagent For example, the reaction with vinyl bromide becomes violent at slightly elevated temperatures, while reactions with dichloro-, trichloro-, and tetrachloro-ethylene have been effected at 100° without a solvent.³⁷⁹ Generally such vigorous conditions are neither necessary nor desirable. The principal product is the nitrochloroalkane, often mixed with smaller amounts of various other adducts, as illustrated above with cyclohexene.

The structure of the nitrochloroalkane can generally be predicted by assuming attack of the $\cdot NO_2$ radical on the least substituted carbon atom of the double bond followed by transfer with nitryl chloride However, other products can arise, apparently as a result of initial attack by a chlorine atom followed by transfer on the nitryl chloride Thus the structures reported for the reaction products from styrene³⁷⁹ and from cinnamic acid,³⁷⁹ viz, α -nitro- β -chloroethylbenzene and α -chloro- β -nitro- β -phenylpropionic acid, respectively could be rationalized on the basis of such a mechanism predominating More study of this possibility seems called for, especially in view of the importance of an analogous chain mechanism in sulfonyl halide additions (See p 204)

There has been little study of the reaction of nitryl chloride with acetylenes. The reaction with phenylacetylene was originally reported to

³⁷⁵ Bachmann and Logan, *J. Org. Chem.*, **21**, 1467 (1956)

³⁷⁹ Steinkopf and Kuhnle, *Ber.*, **75**, 1323 (1942). *Bell. pat.* 448,701 [*C. A.*, **42**, 201 (1948)].

yield α -nitro- β -chlorostyrene,³⁷⁹ but recent work indicates that the major constituent of the "difficulty separable mixture of products" is α -chloro- β -nitrostyrene.³⁶⁹ The only other acetylene to be treated with nitril chloride is dichloroacetylene reported, without details, to give trichloro-nitroethylene.³⁸⁰

The principal point to be considered with respect to reactions of dinitrogen tetroxide/halogen mixtures with olefins is the possible competition between the ionic reaction leading to halonitrates³⁷⁸ and the free radical reaction leading to halonitroalkanes.^{369,375} This is discussed more fully under "Experimental Conditions" below. The free radical reaction has been demonstrated for a moderate number of olefins and for a few acetylenes. With electronegatively substituted olefins, there is no interference from the ionic reaction under any of the conditions studied, but considerable amounts of the *vic*-dihaloalkanes are obtained when mixtures of dinitrogen tetroxide with either chlorine or bromine are used. With iodine, this is not a serious matter, and 50–90% yields of the iodonitroalkanes are easily obtained. The rate of reaction of halogenated ethylenes decreases with increasing number of halogen atoms in the olefins.³⁷⁵ No adduct is obtained with tetrachloroethylene in 72 hours.

With propylene and 1-butene, only dichloroalkanes are obtained in liquid-phase reactions with dinitrogen tetroxide-chlorine mixtures.³⁸¹

Experimental Conditions. The conditions used in effecting addition of nitril chloride to olefins cover a rather wide range. Solvents are generally employed but apparently are not essential in most instances. Among the more effective solvents are chlorinated hydrocarbons, nitromethane, difluorodichloromethane, and diethyl ether. Paraffin-type solvents are less satisfactory and give lower yields.³⁸²

In reaction with isobutylene, a 51% yield of adduct is obtained in the absence of a solvent, a 20% yield in pentane, and a 64% yield in chloroform.³⁸²

An unusual influence of solvent on product mixture is found with acrylonitrile. In the absence of solvent, a 76% yield of α -chloro- β -nitropropionitrile is obtained, while in the presence of diethyl ether this product is obtained in only 25% yield together with β -nitroacrylonitrile in 48% yield.³⁷⁷

The reaction temperatures, in either the presence or absence of solvent, vary mostly between about -20° and $+20^\circ$. The reaction with chlorinated ethylenes appears to require far more vigorous conditions. For example, trichloroethylene is heated in a bomb at 100° for 3 hours to

³⁸⁰ Brintzinger and Pfannstiel, *Z. Anorg. Chem.*, **255**, 325 (1948).

³⁸¹ Bachman and Chupp, *J. Org. Chem.*, **21**, 465 (1956).

³⁸² Himel, U.S. pat. 2,511,915 [*C.A.*, **44**, 8360 (1950)].

obtain a 70% yield of adduct³⁶³ By contrast, vinyl bromide reacts so rapidly with nitryl chloride that cooling of the reaction mixture is essential³⁷³

The reaction of olefins with mixtures of dinitrogen tetroxide and halogen has been shown to proceed in the vapor phase³⁸¹ as well as in the liquid phase^{360,373} Propylene and 1-butene react with dinitrogen tetroxide-chlorine mixtures at 260–275° and a contact time of a few seconds to give low yields of the respective 1-chloro-2-nitroalkanes together with major amounts of the dichloroalkane In the liquid phase at about 0°, only dichloroalkanes are formed³⁸¹ When bromine or iodine is used instead of chlorine, in the liquid phase, β -haloalkyl nitrates are obtained from ethylene and its simple homologs The conditions used involve the addition of the olefin to a chloroform or carbon tetrachloride solution of dinitrogen tetroxide and halogen, at about 0°³⁷⁸ Under identical conditions, electronegatively substituted olefins, especially the haloethylenes, react with dinitrogen tetroxide-halogen mixtures (even where $X_2 = Cl_2$) to give the β -halonitroalkanes³⁶⁵ Thus, under this particular set of conditions, the nature of the product is apparently determined by the structure of the olefin However, if a stream of dinitrogen tetroxide in nitrogen is passed slowly into an ether solution of an olefin and excess iodine, the products are invariably the β -iodonitroalkanes³⁸⁰ This is true for a wide variety of olefins, and, although it has not been reported, it may be presumed that bromine could be substituted for iodine in this scheme to obtain β -bromonitroalkanes.

EXPERIMENTAL PROCEDURES

cis-1-Bromo-2-chlorocyclohexane (Addition of Hydrogen Bromide to 1-Chlorocyclohexene).^{26,27} A solution of 10 g. (0.085 mole) of 1-chlorocyclohexene in 265 g. (3.7 moles) of pentane is placed in a quartz flask fitted with a condenser, a fritted glass gas bubbler, and a magnetic stirrer. The flask is partially immersed in ice water and is irradiated with a Hanovia-S-100 quartz tube mercury vapor lamp for 2 hours while hydrogen bromide is passed through the solution The dried pentane solution, after washing with 10% aqueous sodium carbonate and water, is distilled, to give crude cis-1-bromo-2-chlorocyclohexane (b.p. 91–97°/10 mm., m.p. –11° to –8°) in 88% yield. The crude product, which contains less than 0.4% of the *trans* isomer, is further purified by recrystallization from pure pentane, followed by fractional distillation to give pure cis-1-bromo-2-chlorocyclohexane, b.p. 87.5–88°/7 mm., n_D^{25} 1.5238.

³⁶³ Kuhn, Ger. pat. 739,633 [C.A., 40, 347 (1946)]

1-Bromo-1-hexene (Addition of Hydrogen Bromide to *n*-Butylacetylene in the Presence of Peroxides).³⁵ One mole (82 g.) of *n*-butylacetylene, containing about 0.8 mole % of peroxide, is placed in a 500-ml. three-necked flask equipped with a stirrer, an inlet tube, and a reflux condenser. The flask is cooled in an ice bath, and 1.5 moles of dry hydrogen bromide is passed in rapidly. At the end of 1 hour the reaction mixture is washed with aqueous sodium carbonate followed by water, and dried over anhydrous sodium sulfate. Distillation through an efficient column gives 5 g. of unreacted *n*-butylacetylene, 120 g. (74%) of 1-bromo-1-hexene (b.p. 139–141°/751 mm.; n_D^{20} 1.4596), and 3 g. of 1,2-dibromohexane (b.p. 89–90°/19 mm.; n_D^{20} 1.5024).

When 2.0 moles of hydrogen bromide is passed into 1 mole of *n*-butylacetylene containing 0.6 mole % of peroxides, during 3 hours at ice-bath temperature, the product consists of 85 g. (37%) of 1-bromo-1-hexene and 91 g. (52%) of 1,2-dibromohexane.

Trifluoromethyl 2,2-Difluoroethyl Sulfide (X-Ray-Initiated Addition of Trifluoromethanethiol to 1,1-Difluoroethylene).⁶ A mixture of 27 g. (0.275 mole) of trifluoromethanethiol and 14 g. (0.218 mole) of 1,1-difluoroethylene is loaded into a 100-ml. stainless steel pressure vessel, and the mixture is irradiated with x-rays for 3 hours at an average dose rate of ca. 16,000 rad./min.* Volatiles are bled off and the residue is distilled through a small spinning-band still. There is obtained 26 g. (72%) of trifluoromethyl 2,2-difluoroethyl sulfide distilling at 55–58° (mostly 58°); n_D^{25} 1.3270–1.3276.

3-(2-Methyl)pentyl Thiolacetate (UV-Initiated Addition of Thiolacetic Acid to 2-Methyl-2-pentene).³⁸⁴ Freshly distilled thiolacetic acid (152.2 g., 2 moles) is added slowly with stirring to 336.6 g. (4 moles) of 2-methyl-2-pentene. The reaction mixture is irradiated during the addition with a 100-watt bulb, and irradiation and stirring are continued for an hour after the addition is complete. Distillation of the reaction mixture yields 309 g. (96%) of 3-(2-methyl)pentyl thiolacetate; b.p. 70°/13 mm.; n_D^{25} 1.4603.

3-Acetoxyprop-1-enyl Thiolacetate and 2,3-bis-(Acetylthio)propyl Acetate (Addition of Thiolacetic Acid to Propargyl Acetate).¹⁷⁴ A mixture of 7.4 g. (0.075 mole) of propargyl acetate, 11.4 g. (0.15 mole) of thiolacetic acid, and 0.1 g. of α,α' -azo-bis(isobutyronitrile) contained in a sealed glass tube is irradiated for 24 hours with a 200-watt mercury lamp. Distillation of the reaction mixture yields 1.5 g. (10%) of

* The x-rays were generated by impinging 3-Mev. electrons from a Van de Graaff accelerator on a water-cooled gold target mounted beneath the window of the electron tube. Dose rates were determined by ferrous sulfate dosimetry.

³⁸⁴ Bordwell and Hewett, *J. Org. Chem.*, **22**, 980 (1957).

3-acetoxyprop-1-enyl thiocetate (b p. 95–97°/3 mm; n_D^{18} 1.5115) and 12.0 g. (65%) of 2,3-bis(acetylthio)propyl acetate (b p. 92–95°/0.01 mm; n_D^{18} 1.5181)

2-Phenoxyethanethiol and bis-(2-Phenoxyethyl) Sulfide (Addition of Hydrogen Sulfide to Vinyl Phenyl Ether).²⁰⁰ A mixture of 20 g. (0.166 mole) of vinyl phenyl ether, 12 g. (0.352 mole) of hydrogen sulfide, and 0.04 g. of α, α' -azo-bis(isobutyronitrile) is sealed under vacuum in a glass tube. After 16 days, including 53 hours at 60°, the tube is opened. Upon distillation of the reaction mixture there is obtained 16 g. (62%) of 2-phenoxyethanethiol distilling at 96–100°/4–5 mm; n_D^{20} 1.5600. The residue (7.2 g., 32%) is recrystallized from alcohol to yield bis-(2-phenoxyethyl) sulfide melting at 54.5–55°.

Sodium 1,1,2,3,3,3-Hexafluoropropane-1-sulfonate (Addition of Sodium Bisulfite to Hexafluoropropene).²¹⁵ A mixture of 90 g. (0.6 mole) of hexafluoropropene, 60 g. (0.5 mole) of sodium bisulfite, 27.4 g. of borax, 120 ml. of water, and 0.8 g. of benzoyl peroxide is charged into a stainless steel autoclave. The contents of the autoclave are heated with agitation at 110–120° for 9 hours. The reaction mixture is evaporated to dryness and the residue extracted with hot ethanol. Upon evaporation of the ethanol there is isolated about 115 g. (91%) of crude sodium 1,1,2,3,3,3-hexafluoropropane-1-sulfonate.

***p*-Chlorophenyl 2-Chloroethyl Sulfone** (Addition of *p*-Chlorobenzenesulfonyl Chloride to Ethylene).²²⁹ A mixture of 315 g. (0.67 mole) of *p*-chlorobenzenesulfonyl chloride and 12.3 g. of α, α' -azo-bis(isobutyronitrile) is loaded into a 1250-ml. autoclave. The autoclave is evacuated and ethylene admitted until a pressure of 1500 p.s.i. is attained at 70°. The autoclave is agitated for 24 hours at 70°, the initial pressure being maintained by addition of ethylene, and then vented. The reaction mixture is distilled to yield 74 g. (21%) of crude *p*-chlorophenyl 2-chloroethyl sulfone distilling at 134–163°/0.4–0.6 mm, and 127 g. (32%) of material boiling in the range 163–184°/0.6–0.8 mm, which is chiefly *p*-chlorophenyl 4-chlorobutyl sulfone.

***n*-Octyltrichlorosilane** (Addition of Trichlorosilane to 1-Octene).²⁵⁶ A mixture of 17.9 g. (0.16 mole) of 1-octene and 135.5 g. (1.0 mole) of trichlorosilane (b p. 32°) is placed in a flask fitted with dropping funnel, thermometer, and reflux condenser connected through a –80° trap to a mercury seal 20 cm. in height. The system is swept with nitrogen and the reaction mixture heated to 45° under the slight extra pressure of the mercury. A solution of 3 g. (0.025 mole) of diacetyl peroxide in 19.9 g. (0.17 mole) of 1-octene is added during 2 hours, after which the mixture is heated at 50–63° for an additional 9 hours. Distillation under reduced pressure gives, after removal of excess trichlorosilane,

80.9 g. (99%) of *n*-octyltrichlorosilane, which boils at 231–232°/728 mm. on subsequent redistillation.

Methyl-*n*-propyldichlorosilane (Thermal Addition of Methyl-dichlorosilane to Propylene).²⁵⁸ A mixture of 345 g. (3 moles) of methyl-dichlorosilane and 128 g. (3 moles) of propylene in a 2.4-l. pressure bomb is heated overnight at 300°. The maximum pressure is 1120 p.s.i. Distillation of the reaction mixture gives 340 g. (72%) of methyl *n*-propyldichlorosilane, boiling at 123–124°/747 mm. Some methylhexyldichlorosilane was formed in the reaction.

Diethyl β -Acetoxypropyl Phosphonate (Peroxide-Initiated Addition of Diethyl Phosphite to Isopropenyl Acetate).³³³ A solution of 5 g. of benzoyl peroxide in 93 g. (0.93 mole) of isopropenyl acetate is added during 3 hours to 319 g. (2.30 moles) of diethyl phosphite held at 85–95°. When the addition is complete, an additional 5 g. of benzoyl peroxide is added and heating is continued for another hour. After removal of the excess diethyl phosphite under reduced pressure, the residual oil is distilled. The fraction boiling at 78–100°/0.50 mm yields on redistillation 160 g. (72%) of diethyl β -acetoxypropyl phosphonate, b.p. 89–93°/0.05 mm., n_D^{25} 1.4301.

Fractionation of the higher-boiling fractions yields about 25 g. of a substance containing 2 units of isopropenyl acetate to 1 of diethyl phosphite, b.p. 100–115°/0.01 mm., n_D^{25} 1.4461.

1-Nitro-2-propyl Iodide (Addition of Dinitrogen Tetroxide to Propylene).³⁶⁰ Dinitrogen tetroxide (6.9 g.; 0.15 mole as NO_2) in a stream of dry nitrogen is passed into a cold (0°) stirred solution of 30 ml. of propylene and 31 g. (0.25 mole) of iodine in 200 ml. of diethyl ether during 2 hours. The reaction system is protected by a solid carbon dioxide-acetone condenser and a drying tube. Stirring is continued for 1 hour at 0° after the addition of the dinitrogen tetroxide. The ether solution is washed with 15% aqueous sodium thiosulfate until colorless, then with aqueous sodium bicarbonate and water, and dried over magnesium sulfate. The residue remaining after evaporation of the ether at 30 mm. pressure is distilled through a brown glass distilling head to give 22.5 g. (70%) of 1-nitro-2-propyl iodide, b.p. 40–42°/0.5 mm. Redistillation gives 1.7 g. of fore-run (b.p. 42–44°/0.45 mm.; n_D^{20} 1.5370) and 18.4 g of 1-nitro-2-propyl iodide (b.p. 44°/0.45 mm., n_D^{20} 1.5378).

2-Chloro-3-nitropropionic Acid (Reaction of Nitryl Chloride with Acrylic Acid).³⁷⁷ Nitryl chloride (85 g., 1.05 mole; 20% excess) is distilled through a gas delivery tube into 64 g. (0.89 mole) of glacial acrylic acid at 0°. The orange-red mixture is stirred at room temperature for an hour, and excess nitryl chloride is then removed under reduced pressure. The syrupy product crystallizes slowly at 0–5° to a white solid

(109 g., 71%). A 20-g. sample of this material is dissolved in benzene, the solution separated from an insoluble residue (1.5 g.) and concentrated until precipitation occurs. Filtration gives a white solid (11.4 g.), m.p. 72–74°, which when recrystallized from benzene yields 2-chloro-3-nitropropionic acid, m.p. 78–80°.

Distillation of the crude reaction product at 0.7 mm. pressure results in dehydrochlorination of the 2-chloro-3-nitropropionic acid to 3-nitroacrylic acid, m.p. 136°.

1,2-Dinitro-2,4,4-trimethylpentane and 1-Nitro-2,4,4-trimethyl-2-pentanol (Addition of Dinitrogen Tetroxide to 2,4,4-Trimethyl-1-pentene).^{37a} 2,4,4-Trimethyl-1-pentene (332 g.) is added dropwise during 3 hours to a well-stirred solution of 790 g. of dinitrogen tetroxide in 1830 g. of dry diethyl ether at –5°. Solvent and excess tetroxide are then removed, and the product, a yellow oil, is stirred with two 600-ml. portions of water for 20 minutes to hydrolyze the nitro-nitrite. After the oil has stood with water overnight, it is separated and dried by azeotropic distillation with benzene. Fractional distillation of the dried oil (610 g.) gives (i) 169 g., b.p. 52–68°/0.5 mm., (ii) 339 g., b.p. 80–130°/1 mm., and (iii) a residue of 54 g.

Redistillation of (i) gives 163 g. (31%) of 1-nitro-2,4,4-trimethyl-2-pentanol, b.p. 58–62°/1 mm.

Redistillation of fraction (ii) gives a center cut of 320 g. (53%) of 1,2-dinitro-2,4,4-trimethylpentane, b.p. 94–102°/1 mm.

TABULAR SURVEY

The unsaturates are tabulated according to increasing number of carbon atoms following the system used in *Chemical Abstracts*. Where necessary, the addends have also been arranged according to increasing number of carbon atoms. The silanes in Table XI-C and the phosphines in Table XIII have been arranged in order of decreasing number of hydrogen atoms on the hetero atom.

A dash in the yield column indicates that no yield was reported.

The literature survey included *Chemical Abstracts* index through 1960. Although no exhaustive search of the 1961–early 1962 literature was possible, all the papers encountered in the readily available journals are included.

TABLE IX

HYDROHALOGENATIONS

A. Addition of Hydrogen Bromide to Olefins

Olefin	Catalyst	Product (Yield, %)	Refs.
$\text{CF}_2=\text{CFCl}$	UV	$\text{CF}_2\text{BrCH}_2\text{FCl}$ (88)	385
$\text{CF}_2=\text{CF}_2$	UV	$\text{CF}_2\text{BrCH}_2\text{F}_2$ (66)	385
$\text{CCl}_2=\text{CHCl}$ (+ DBr)	Peroxide (UV)	$\text{CCl}_2\text{CH}_2\text{CHClBr}$ (nearly quant.)	386
$\text{CCl}_2=\text{CHCl}$	Peroxide	$\text{CHCl}_2\text{CHClBr}$ (90)	58
$\text{CF}_2=\text{CHCl}$	UV	$\text{CF}_2\text{BrCH}_2\text{Cl}$ (99)	4
$\text{CF}_2=\text{CHF}$	UV	$\text{CHF}_2\text{CH}_2\text{FBr}$ (57)	5
		$\text{CF}_2\text{BrCH}_2\text{F}$ (43)	
$\text{CCl}_2=\text{CH}_2$ (+ DBr)	UV	$\text{CCl}_2\text{CH}_2\text{Br}$ (64)	22
		$\text{CCl}_2\text{CH}_2\text{CCl}_2\text{CH}_2\text{Br}$	
$\text{CCl}_2=\text{CH}_2$	UV	$\text{CHCl}_2\text{CH}_2\text{Br}$ (62)	22
		$\text{CHCl}_2\text{CH}_2\text{CCl}_2\text{CH}_2\text{Br}$ (32)	
$\text{CF}_2=\text{CH}_2$	UV	$\text{CHF}_2\text{CH}_2\text{Br}$ (85)	387
$\text{CHBr}=\text{CH}_2$	None added	$\text{CH}_2\text{BrCH}_2\text{Br}$ (92)	388
(+ DBr)	Light	$\text{CHDBrCH}_2\text{Br}$ (—)	389
$\text{CDBr}=\text{CH}_2$ (+ DBr)	Light	$\text{CD}_2\text{BrCH}_2\text{Br}$ (—)	389
$\text{CHBr}=\text{CD}_2$	Light	$\text{CH}_2\text{BrCD}_2\text{Br}$ (—)	389
$\text{CDBr}=\text{CD}_2$	Light	$\text{CHDBrCD}_2\text{Br}$ (—)	389
$\text{CHCl}=\text{CH}_2$	Peroxide	$\text{CH}_2\text{ClCH}_2\text{Br}$ (79)	390
	UV	$\text{CH}_2\text{ClCH}_2\text{Br}$ (68)	391
$\text{CF}_3\text{CF}=\text{CF}_2$	Light	$\text{CF}_3\text{CHF}_2\text{CF}_2\text{Br}$ (88)	392
	X-rays or UV	$\text{CF}_3\text{CHF}_2\text{CF}_2\text{Br}$ (47)	44
		$\text{CF}_3\text{CFBrCH}_2\text{F}_2$ (29)	
$\text{CF}_3\text{CH}=\text{CF}_2$	UV	$\text{CF}_3\text{CH}_2\text{CF}_2\text{Br}$ (40)	393
$\text{CCl}_3\text{CCl}=\text{CH}_2$	Peroxide	$\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Br}$ (ca. 30)	52
		$\text{CCl}_3=\text{CClCH}_2\text{Br}$	




$\text{CCl}_3\text{CH}=\text{CH}_2$	Peroxide	$\text{CHCl}_2\text{CHClCH}_2\text{Br}$ (77)	50
$\text{CHCl}_2\text{CCl}=\text{CH}_2$	Peroxide	$\text{CHCl}_2\text{CHClCH}_2\text{Br}$ (ca 20)	52
$\text{CFCl}_2\text{CH}=\text{CH}_2$	UV	$\text{CFCl}_2\text{CH}_2\text{CH}_2\text{Br}$ (38)	57
$\text{CF}_2\text{CH}=\text{CH}_2$	UV	$\text{CHFClCHClCH}_2\text{Br}$ (18)	394, 395
$\text{CHCl}_2\text{CH}=\text{CH}_2$	Peroxide	$\text{CF}_2\text{CH}_2\text{CH}_2\text{Br}$ (90-97)	55, 56
$\text{CH}_3\text{CH}=\text{CF}_2$	UV	$\text{CHCl}_2\text{CH}_2\text{CH}_2\text{Br}$ (5)	42
$\text{CH}_2\text{BrCH}=\text{CH}_2$	Oxygen	$\text{CH}_3\text{CHClCHCl}_2\text{Br}$ (45)	12
$\text{CH}_2\text{BrCH}=\text{CH}_2$	Ni or Fe	$\text{CH}_3\text{CHBrCHF}_2$ (93)	61, 16
	Oxygen	$\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$ (90)	20
	UV	$\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$ (37-38)	11
	Peroxide	$\text{CH}_2\text{BrCHBrCH}_3$ (2-3)	9
	Peroxide	$\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$ (20-60)	9
	Peroxide	$\text{CH}_2\text{BrCHBrCH}_3$ (5-10)	9
	Peroxide	$\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Br}$ (95)	9
	Peroxide	$\text{CH}_2\text{CHBrCH}_2\text{Br}$ (66)	37
	Peroxide	$\text{CH}_3\text{CBBrCH}_3$ (14)	396, 397
	Peroxide	$\text{CH}_3\text{CHBrCH}_2\text{Br}$ (84)	13, 398
	Peroxide	$\text{CH}_3\text{CHClCH}_2\text{Br}$ (74)	391, 11
	Peroxide	$\text{CH}_3\text{CClBrCH}_3$ (26)	60, 11
	Peroxide	$\text{CH}_3\text{CHBrCH}_2\text{Cl}$ (90)	399, 14
	Peroxide	$\text{Cl}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{Br}$ (87)	387
	Peroxide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (78)	387
	Peroxide	$\text{CH}_3\text{CHBrCH}_3$ (12)	
	Peroxide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (quant.)	
	Peroxide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (quant.)	
	Peroxide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (60)	
	Peroxide	$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ (98)	
	Peroxide	$\text{CF}_3\text{CHFCFBrCF}_2$ (60)	
	Peroxide	$\text{CF}_2\text{CHFCFBrCF}_2$ (33)	

Note. References 385 to 631 are on pp. 371-376.

TABLE IX—Continued

A. Addition of Hydrogen Bromide to Olefins—Continued

Olefin	Catalyst	Product (Yield, %)	Refs.
$(CF_3)_2C=CH_2$	UV	$(CF_3)_2CHCH_2Br$ (93)	42
$CH_2ClBr-CH=CHCH_3$	UV	$CH_2ClBr-CHBrCH_2Br$ <i>cis</i> (72)	28
$\underbrace{CH_2ClBr-CH=CHCH_3}_{CCl_3C(CH_3)=CH_2}$		$\underbrace{CH_2ClBr-CHBrCH_2Br}_{trans}$ (18)	
$CCl_3C(CH_3)=CH_2$	Peroxide	$CHCl_2CCl(CH_3)CH_2Br$ (—)	51
$CH_3CCl_2CH=CH_2$	Peroxide	$Cl_2C=C(CH_3)CH_2Br$ (—)	
$CHCl_2C(CH_3)=CH_2$	Peroxide	$CH_3CHClCHClCH_2Br$ (73)	55
$CH_3CH=CHCH_2$	Peroxide	$CHCl_2CH(CH_3)CH_2Br$ (34)	55, 53
$CH_3CH=CHCH=CH_2$	Peroxide	$CH_2ClCCl(CH_3)CH_2Br$ (30)	
$CH_3CH=CHCO_2H$	*	$CH_3CH=CHCH_2Br$ (44-76)	400
$CH_3CHBrCH=CH_2$	Peroxide	$CH_2=CHCHBrCH_3$ (56-24)	401, 402
$CH_3CHBrCH=CH_2$	Peroxide	$CH_3CHBrCH_2CH_2Br$ (83)	400
$CH_2BrCH=CHCH_3$	Peroxide	$CH_3CHBrCHBrCH_3$ (17)	
$cis-CH_3CH=CHCH_3$	Peroxide	$CH_2BrCH_2CHBrCH_3$ (78)	400
$trans-CH_3CH=CHCH_3$	UV	$CH_3CHBrCHBrCH_3$ (16)	
$trans-CH_3CH=CHCH_3$	UV	<i>meso</i> - $CH_3CHBrCHBrCH_3$ (92)	403
$trans-CH_3CH=CHCH_3$	UV	<i>d,l</i> - $CH_3CHBrCHBrCH_3$ (5)	
$CH_3CH_2CH=CH_2$	Peroxide	<i>meso</i> - $CH_3CHBrCHBrCH_3$ (9)	403
	UV	<i>d,l</i> - $CH_3CHBrCHBrCH_3$ (83)	
	Bromoacetone	$CH_3CH_2CH_2CH_2Br$ (95)	404
	Silent discharge	$CH_3CH_2CH_2CH_2Br$ (99)	11, 391
		$CH_3CH_2CH_2CH_2Br$ (quant.)	13, 398
		$CH_3CH_2CH_2CH_2Br$	14

$(CH_3)_2C=CH_2$	Peroxide	$(CH_3)_2CHCH_2Br$ (91)	405, 406
<i>cis</i> - $CH_2CH=CHCH_2$ (+ DBr)	UV	$(CH_3)_2CBrCH_2$ (6)	391
<i>trans</i> - $CH_2CH=CHCH_2$ (+ DBr)	Light	$(CH_3)_2CHCH_2Br$ (80)	23
$Cl_2(CH_3)_2SiCH_2CH=CH_2$	Light	<i>threo</i> - $CH_2CH_2CH(Cl)CH_2CH_3$ (95)	23
$Cl_2SiCH_2C(CH_3)=CH_2$	Peroxide	<i>erythro</i> - $CH_2CH_2CH(Cl)CH_2CH_3$ (quant.)	37
$(CF_3)_2C=CHCO_2H$	Peroxide	$Cl_2CH_2C(CH_3)_2Br$ (72)	37
	Peroxide (UV)	$Cl_2SiCH_2C(CH_3)_2Br$ (85)	37
		$(CF_3)_2CHCHBrCO_2H$ (97)	407
	UV	 <i>cis</i> (91)	29
		 <i>trans</i> (6)	
$CH_2=CHCH_2CH_2CO_2H$	Peroxide	$CH_2BrCH_2CH_2CH_2CO_2H$ (80, 100)	409
$CH_2=C(CH_3)CO_2CH_3$	*	$CH_2BrCH(CH_3)CO_2CH_3$ (quant.)	409
$CH_3CH_2CH_2CH=CH_2$	Peroxide	$CH_3CH_2CH_2CH_2Br$ (96)	410
$CH_3CH_2CH=CHCH_3$	*	$CH_3CH_2CH_2CH_2CH_2CH_3$ (36)	411
$(CH_3)_2CHCH=CH_2$	Peroxide	$CH_3CH_2CH_2CH_2CH_2CH_3$ (36)	
		$(CH_3)_2CHCH_2CH_2Br$ (80)	412
$(CH_3)_2C=CHCH_3$	Peroxide	$(CH_3)_2CHCH_2CH_2CH_3$ (13, 6)	
		$(CH_3)_2CHCH_2CH_2CH_3$ (6, 4)	
$Cl(CH_3)_2SiCH_2CH=CH_2$	Peroxide	$(CH_3)_2CHCH_2CH_2CH_3$ (43)	
$(CH_3)_2SiCH=CH_2$	Peroxide	$(CH_3)_2CHCH_2CH_2CH_3$ (24)	
	Peroxide	$Cl(CH_3)_2SiCH_2CH_2CH_3$ (82)	
		$(CH_3)_2SiCH_2CH_2Br$ (79)	37
			413

Note. References 385 to 631 are on pp. 371-376.

* The same product was obtained with or without added peroxide.

TABLE IX—Continued


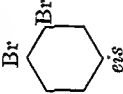

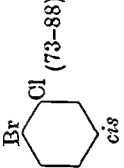
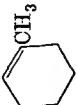
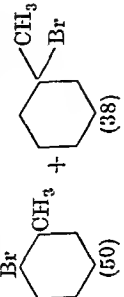
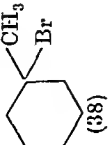
A. Addition of Hydrogen Bromide to Olefins—Continued			
Olefin	Catalyst	Product (Yield, %)	Refs.
$\text{CF}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$	*	$\text{CF}_3\text{CHBrCH}_2\text{CO}_2\text{C}_2\text{H}_5$ (—)	414
	UV	 (76-81)	26, 27
	UV or peroxido	 (73-88)	27
$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}=\text{CH}_2$	UV	$\text{Br}(\text{CH}_2)_6\text{Br}$ (quant.)	11
	None added	$\text{CH}_2\text{Br}(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (21)	415
		$\text{CH}_3\text{CHBr}(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (26)	
$\text{CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$\text{CH}_3\text{CHBrCH}_2\text{CO}_2\text{C}_2\text{H}_5$	401
$\text{C}_4\text{H}_9\text{CB}r=\text{CH}_2$	Peroxido	$\text{C}_4\text{H}_9\text{CHBrCH}_2\text{Br}$ (84)	35
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$	Silont discharged	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{Br}$ (68)	14
$(\text{CH}_2)_3\text{SiCH}_2\text{CH}=\text{CH}_2$	Peroxido	$(\text{CH}_2)_3\text{SiCH}_2\text{CHBrCH}_3$ (73)	36
$(\text{CH}_3)_3\text{CCCH}_2\text{CH}=\text{CH}_2$	Peroxido	$(\text{CH}_3)_3\text{CCCH}_2\text{CH}_2\text{Br}$ ("High")	416
	UV	 (50) +  (38)	26

TABLE IX—Continued

A. Addition of Hydrogen Bromide to Olefins—Continued

Olefin	Catalyst	Product (Yield, %)	Refs.
$\text{CH}_3\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	Peroxide	$\text{CH}_3\text{CH}_2\text{CHBr}(\text{CH}_2)_7\text{CO}_2\text{H}$ } [†] $\text{CH}_3\text{CHBr}(\text{CH}_2)_8\text{CO}_2\text{H}$	421
$\text{CH}_3(\text{CH}_2)_{10}\text{CH}=\text{CH}_2$	Peroxide	$\text{CH}_3(\text{CH}_2)_{11}\text{CH}_2\text{Br}$ (85)	15
$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CO}_2\text{C}_2\text{H}_5$	Peroxide	$\text{Br}(\text{CH}_2)_{10}\text{CO}_2\text{C}_2\text{H}_5$ (80) [†]	422
$\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{OCOCH}_3$	Peroxide	$\text{Br}(\text{CH}_2)_{11}\text{OCOCH}_3$ (—)	422
$\text{CH}_3(\text{CH}_2)_{12}\text{CH}=\text{CH}_2$	Peroxide	$\text{CH}_3(\text{CH}_2)_{13}\text{CH}_2\text{Br}$ (60)	15
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$	UV	9-Bromo-acid } [†] 10-Bromo-acid	423
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{CH}_3$	UV	9-Bromo ester } [†] 10-Bromo ester	423
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_6\text{H}_5$	Peroxide	9-Bromo ester } [†] 10-Bromo ester	423
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_6\text{H}_4\text{NO}_2$ -p	Peroxide	9-Bromo ester } [†] 10-Bromo ester	423
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_6\text{H}_4\text{OCH}_3$ -p	Peroxide	9-Bromo ester } [†] 10-Bromo ester	423

B. Addition of Hydrogen Bromide to Acetylenes

Acetylene	Catalyst	Product (Yield, %)	Refs.
DC≡CD	Light	CHD=CDBr (—)	389
(+ DBr)	Light	CHDBrCHDBr (—)	389
(+ DBr)	UV	CD ₂ =CDBr (—)	424
HC≡CH	Light	CD ₂ BrCD ₂ Br (—)	389
(+ DBr)	Light	CD ₂ BrCD ₂ Br (quant.)	
		CH ₂ =CHBr (—)	
		CH ₂ BrCH ₂ Br (—)	
		CHD=CHBr (—)	389
CH ₃ C≡CBr	UV	CHDBrCHDBr (—)	
CF ₃ C≡CH	UV	CH ₃ CB=CHBr (75% <i>trans</i>) (92)	32
CH ₃ C≡CH	Peroxide	CF ₃ CH=CHBr (—)	39
	Light	CH ₃ CHBrCH ₂ Br (95-100)	41
		<i>cis</i> -CH ₃ CH=CHBr (70)	30
	UV	CH ₃ CHBrCH ₂ Br (30)	
	Peroxide	CF ₃ CH=CBBrCF ₃ (87)	39
		<i>d,l</i> CH ₃ CHBrCHBrCH ₃ (86)	31
(CH ₃) ₂ CO≡CBr	UV	CH ₃ CH ₂ CHBrCH ₂ CH ₃ (4)	
<i>n</i> -C ₄ H ₉ C≡CH	Peroxide	<i>trans</i> -(CH ₃) ₂ CCBr=CHBr (89)	32
		<i>n</i> -C ₄ H ₉ CH=CHBr (74-52)	35
		<i>n</i> -C ₄ H ₉ CHBrCH ₂ Br (trace-37)	
		<i>trans</i> -C ₄ H ₉ CH=CBBrCO ₂ H§ (95)	33
		CHBr=CH(CH ₂) ₃ CO ₂ H	40

Note. References 385 to 631 are on pp 371-376.

† Equal amounts of the two isomers were obtained

‡ The product was isolated as the *o*-hydroxy acid

§ The formation of this product was inhibited by catechol; hence a radical path was assumed

TABLE IX—Continued
C. Addition of Hydrogen Chloride to Olefins





Olefin	Catalyst	Product (Yield, %)	Rofs.
$\text{CH}_3=\text{CH}_2$	Peroxido	$\text{H}(\text{CH}_2\text{CH}_2)_n\text{Cl}$	49, 425
		n (%)	
		2 (6)	
		7 (5)	
		3 (6)	
		8 (6)	
		4 (9)	
		9 (6)	
		5 (9)	
		10 (5)	
		6 (8)	
		> 10 (40)	
$\text{CH}_2\text{ClCH}=\text{CH}_2$	Peroxido	$\text{CH}_2\text{ClCHClCH}_2\text{Cl}$ (22)	48
		$\text{CH}_2\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (9)	
		2:1 adduct	
$\text{CH}_3\text{CH}=\text{CH}_2$	Peroxido	$\text{CH}_3\text{CHClCH}_2\text{Cl}$ (27)	48
		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ (4)	
$(\text{CH}_3)_3\text{CCH}=\text{CH}_2$	Peroxido	$(\text{CH}_3)_3\text{CHClCH}(\text{CH}_3)_2$ (5)	47
		$(\text{CH}_3)_3\text{CCHClCH}_2\text{Cl}$ (71)	
		$(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Cl}$ (24)	

Note: References 385 to 631 are on pp. 371–376.

TABLE X



FORMATION OF CARBON-SULFUR BONDS




A. Addition of Aliphatic Thiols to Olefins

Thiol	Olefin	Catalyst	Products (%)	Refs
CH_3SH	$\text{CF}_2=\text{CF}_2$	UV	$\text{CH}_2\text{SCF}_2\text{CHFCF}_2$ (84) $\text{CH}_2\text{S}(\text{CF}_2\text{CF}_2)_2\text{H}$ (5) $\text{CH}_2\text{SCHFCF}_2$ (45)	6
	$\text{CHF}=\text{CF}_2$	X-ray	$\text{CH}_2\text{SCF}_2\text{CH}_2\text{F}$ (15)	6
	$\text{CH}_2=\text{CHCl}$	UV + O_2	$\text{CH}_2\text{S}(\text{CH}_2)_2\text{Cl}$ (92-95)	120, 426
	$\text{CH}_2=\text{CH}_2 + \text{CO}$ (1000-2000 atm.)	Peroxide	$\text{CH}_2\text{SCH}_2\text{CH}_2\text{CHO}$ (18) $\text{CH}_2\text{SC}_2\text{H}_5$ (30)	81, 427
	$\text{CF}_3\text{CF}=\text{CF}_2$	X-ray	$\text{CH}_2\text{SCF}_2\text{CHFCF}_3$ (10) $\text{CH}_2\text{SCF}(\text{CF}_3)\text{CHF}_2$ (1)	6
	$\text{CH}_2=\text{CHCHO}$	Peroxide	$\text{CH}_2\text{S}(\text{CH}_2)_2\text{CHO}$ (66)	428, 429, 183, 430-432 183
	$\text{CH}_2=\text{CHCO}_2\text{H}$	UV, O_2 + $\text{Hg}(\text{SCH}_3)_2$	$\text{CH}_2\text{S}(\text{CH}_2)_2\text{CO}_2\text{H}$ (—)	433, 434, 426
	$\text{CH}_2=\text{CHCH}_2\text{OH}$	UV, O_2 + $(\text{CH}_3\text{S})_2\text{H}_2$	$\text{CH}_2\text{S}(\text{CH}_2)_2\text{OH}$ (93-95)	183
	CHCO_2H CHCO_2H	UV, O_2 + a mercuric salt	$\text{CH}_2\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ (—)	
		None added	 (63)	435
	$\text{CH}_2\text{CH}=\text{CHCHO}$ $\text{CH}_2\text{CO}_2\text{CH}=\text{CH}_2$ $\text{CH}_2\text{CH}=\text{CHCO}_2\text{H}$	Peroxide UV + O_2 Peroxide	$\text{CH}_2\text{SCH}(\text{CH}_2)_2\text{CH}_2\text{CHO}$ (67) $\text{CH}_2\text{CO}_2\text{CH}(\text{CH}_2)_2\text{SCH}_3$ (93-95) $\text{CH}_2\text{SCH}(\text{CH}_2)_2\text{CH}_2\text{CO}_2\text{H}$ (60)	113 120, 426 113
		UV + acetone	 (60)	182

Note: Products 345 to 63 are on pp. 371-376

TABLE X—Continued
A. Addition of Aliphatic Thiols to Olefins—Continued

Thiol	Olefin	Catalyst	Products (%)	Refs.
CH_3SH (contd.)		UV, peroxide + diphenyl disulfide	 (70)	109
	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	UV, O_2 + a mercuric salt	$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{SCH}_3$ (—)	183
	$\text{C}_6\text{H}_5\text{COCH}=\text{CHCO}_2\text{H}^a$	None	$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}(\text{SCH}_3)\text{CO}_2\text{H}$ (—)	122
	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$	Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4(\text{CH}_2)_2\text{SCH}_3$ (—)	436
	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$	Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{SCH}_3$ (—)	436
CF_3SH	$\text{CF}_2=\text{CFCl}$	UV	$\text{CF}_3\text{SCF}_2\text{CHFCl}$ (62)	6
			$\text{CF}_3\text{S}(\text{CF}_2\text{CFCI})_2\text{H}$ (20)	
			$\text{CF}_3\text{S}(\text{CF}_2\text{CFCI})_3\text{H}$ (3)	
	$\text{CF}_2=\text{CF}_2$	X-ray	$\text{CF}_3\text{S}(\text{CF}_2)_2\text{H}$ (53)	6
			$\text{CF}_3\text{S}(\text{CF}_2)_4\text{H}$ (17)	
			$\text{CF}_3\text{S}(\text{CF}_2)_6\text{H}$ (4)	
	$\text{CHF}=\text{CF}_3$	UV	$\text{CF}_3\text{SCH}_2\text{CHF}_2$ (83)	6
			$\text{CF}_3\text{SCF}_2\text{CH}_2\text{F}$ (trace)	
			$\text{CF}_3\text{S}(\text{CH}_2\text{CF}_2)_2\text{H}$ (3.5)	
	$\text{CH}_2=\text{CF}_2$	X-ray	$\text{CF}_3\text{SCH}_2\text{CHF}_2$ (72)	6
	$\text{CF}_3\text{CF}=\text{CF}_2$	UV or x-ray	$\text{CF}_3\text{SCF}_2\text{CHF}_2$ (25)	6
			$\text{CF}_3\text{SCF}(\text{CF}_3)\text{CHF}_2$ (31)	
			$\text{CF}_3\text{S}(\text{CF}_2\text{CF}_3)\text{CF}_2\text{SCH}_3$ (13)	
	$\text{CF}_2=\text{CFOCH}_3$	UV	$\text{CF}_3\text{SCF}_2\text{CH}_2\text{FOCH}_3$ (71)	6
	$\text{CF}_2=\text{CF}_2$	Peroxide	1:1 adduct + higher tolomers ^b	87
	$\text{CH}_2=\text{CH}_2$ + CO (2900–3000 atm.)	Peroxide	$\text{C}_2\text{H}_5\text{S}(\text{CH}_2)_2\text{CHO}$ (11)	427, 81
			$\text{C}_2\text{H}_5\text{S}(\text{CH}_2)_2\text{CH}(\text{SC}_2\text{H}_5)_2$ (11)	
			$(\text{C}_2\text{H}_5)_2\text{S}$ (43)	
	$\text{CH}_2=\text{CHCH}_3$	None added	$\text{C}_2\text{H}_5\text{SC}_3\text{H}_{7-n}$ (64)	88, 177,
				437, 438
	$\text{CH}_2=\text{CHCH}_3$ + CO (2900–3000 atm.)	Peroxide	$\text{C}_2\text{H}_5\text{SC}_3\text{H}_{7-n}$ (50)	427, 81
	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	Peroxide + FeCl_2	1:1 adduct ^c	177, 437
			2:1 thiol:olefin adduct ^c	

	None added	$C_2H_5SCH_2CH(CH_3)_2$ (44)	435
$CH_2=CHCO_2CH_3$	Peroxide + UV	$C_2H_5S(CH_2)_2CO_2CH_3$ (37)	69
$CH_2=C(CH_3)_2$	None added	$C_2H_5SCH_2CH(CO_2CH_3)(CH_3)_2$ (23)	88
$CH_2=CHOC_2H_5$	None added	$C_2H_5SCH_2CH(CH_3)_2$ (34)	439
$CH_2=CHSC_2H_5$	O_2	$C_2H_5SCH_2CH_2SC_2H_5$ (93)	179
$CH_2=CHS(CH_2)_2OH$	None added	$C_2H_5S(CH_2)_2S(CH_2)_2OH$ (84) ^a	440
$CH_2=CHCH(CH_3)_2$	None added	$C_2H_5S(CH_2)_2CH(CH_3)_2$ (8)	58
$CH_2=CH=C(CH_3)_2$	None added	$C_2H_5SCH_2CH(CH_3)CH(CH_3)_2$ (60)	88
$CH_2=C(CH_3)SC_2H_5$	None added	$C_2H_5SCH_2CH(CH_3)SC_2H_5$ (80)	441
	Peroxide	 (40)	67
$CH_2=CHOC_2H_5$ ^a	None added	$C_2H_5S(CH_2)_2OC_2H_5$ ^a (97)	439
$C_4H_7OCH=CHSC_2H_5$	Azonitrile	$C_4H_7S(CH_2)_2OC_2H_5$ ^a (98) ^b	442
$CH_2=C(OC_2H_5)_2$ ^a C_2H_5	None added	$C_2H_5OCH(SC_2H_5)CH_2SC_2H_5$ (70)	106
$CH_2=CHSC_2H_5$ ^a	None added	$C_2H_5SCH_2CH(OC_2H_5)SC_2H_5$ (90)	108
$CH_2=C(SC_2H_5)_2$	Peroxide	$C_2H_5SCH_2CH_2SC_2H_5$ ^a (100)	443
$CH_2=CHCH(CH_3)CH_3$	None added	$C_2H_5SCH_2CH(SC_2H_5)_2$ (72-81)	444
$CH_2COSCH=CHCH_2OCOCCH_3$	None added	$C_2H_5S(CH_2)_2S(CH_2)_2$ (61)	445
$CH_2CH=C(SC_2H_5)_2$	Azonitrile + UV	$CH_2OSCH_2CH(SC_2H_5)CH_2OCOCCH_3$ (37)	174
$CH_2=CHC_2H_5$ ^a	Peroxide	$C_2H_5SCH_2CH_2CH(SC_2H_5)_2$ (65)	444
$CH_2=CHC_2H_5$ ^a	Peroxide	$C_2H_5SC_2H_5$ ^a (29)	67

Note. References 285 to 331 are on pp. 373-376.

^a The acid was dissolved in aqueous sodium bicarbonate.

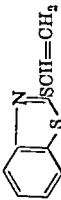
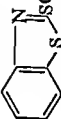




^b The structure was not determined.





^c No yield or structure was given for this adduct.

^d The product contained 12-14% of the normal adduct, $C_2H_5SCH_2CH_2S(CH_2)_2OH$.

^e The product contained 2% of the normal adduct, $C_2H_5SCH_2CH_2OC_2H_5$.

TABLE X—Continued
A. Addition of Aliphatic Thiols to Olefins—Continued






Thiol	Olefin	Catalyst	Products (%)	Refs.
C_3H_7SH (contd.)		Azonitrilo	 $SCH_2CH_2SC_2H_5$ (—)	446
	$CH_2=CHSC_4H_9CH_3$ $CH_2CH=CHSC_4H_9$	None added	$C_2H_5S(CH_2)_2SC_4H_9CH_3$ (—)	447
	$CH_2=CHCH_2SC_4H_9$	Azonitrilo	$C_2H_5SCH(CH_2)_2SC_4H_9$ (82)	448
	$3,4-CH_2O_2C_6H_4CH_2CH=CH_2$	Azonitrilo	$C_2H_5SCH_2CH(CH_2)_2SC_6H_4$ (81)	448
	$3,4-CH_2O_2C_6H_4CH=CHCH_3$	Peroxido	$3,4-CH_2O_2C_6H_4(CH_2)_2SC_2H_5$ (—)	436
	$n-C_4H_9O_2C_6H_4CH=CHCH_3$	Peroxido	$3,4-CH_2O_2C_6H_4CH_2CH(CH_2)_2SC_2H_5$ (—)	436
	$n-C_4H_9CH=CH(SC_2H_5)_2$	Azonitrilo	$n-C_4H_9CH(SC_2H_5)_2CH(SC_2H_5)_2$ (8)	444
	$CH_2=CH(C_4H_9)_2$	UV, or $FeCl_3$ + peroxido	$C_2H_5SC_4H_9$ (94-97)	177, 437, 438, 449, 450
$ClCH_2CH_2SH$		Peroxido + $CrCl_3$	 SCH_2CH_2Cl (—)	177, 437, 438
CF_3CH_2SH	$CF_3CF=CF_2$	UV	$CF_3CH_2SCF_2CH_2CF_3$ (46)	6
$HOCH_2CH_2SH$	$CH_2=CHCl$	$(n-C_4H_9)_2S_2$ + UV	$CF_3CH_2SCH(CF_3)CH_2CF_3$ (20) $HOCH_2CH_2SCH_2CH_2Cl$ (100)	185, 451
	$CH_2=CHCN$	None added	$HOCH_2CH_2SCH_2CH_2CN$ (91)	452
	$CH_2=CHCH_2OH$	None added	$HOCH_2CH_2SCH_2CH_2OH$ (50)	453, 454
	$CH_3CO_2CH=CH_2$	None added	$CH_3CO_2CH_2CH_2SCH_2CH_2OH$ (51)	455
		None added	 SCH_2CH_2OH (—)	453
	$CH_2=CHSCH_2$		$HO(CH_2)_2S(CH_2)_2SCH_2$ $HO(CH_2)_2S(CH_2)_2OCH_2$ (—)	440
	$CH_2=CHOCH_2$	None added	$3,4-CH_2O_2C_6H_4CH_2CH_2SCH_2CH_2OH$ (—)	436
	$3,4-CH_2O_2C_6H_4CH_2CH=CH_2$	Peroxido	$3,4-CH_2O_2C_6H_4CH_2CH(CH_2)_2SCH_2CH_2OH$ (—)	436
	$CH_2=CH(C_4H_9)CO_2H$	None added	$HO(CH_2)_2S(CH_2)_2CO_2H$ (—)	456

$n\text{-C}_3\text{H}_7\text{SH}$	$\text{CH}_3=\text{CHCH}_3$	UV or UV + $(\text{C}_2\text{H}_5)_3\text{Pb}$ <i>t</i> -Butyl hydro- peroxide + $\text{Fe}(\text{NH}_4\text{SO}_4)_2$	$(n\text{-C}_3\text{H}_7)_2\text{S}$ (96)	457, 458
	$\text{CH}_3=\text{CHCH}=\text{CH}_2$		$n\text{-C}_3\text{H}_7\text{SC}_2\text{H}_4\text{OC}_2\text{H}_5$ (63) $n\text{-C}_3\text{H}_7\text{SC}_2\text{H}_4\text{SC}_2\text{H}_5$ (10) $n\text{-C}_3\text{H}_7\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (16) $g\text{-C}_3\text{H}_7\text{OC}_2\text{H}_4\text{H}_2\text{O}$ (5)	459
	$\text{CH}_3\text{COCH}=\text{CH}_2$ $\text{CH}_3=\text{CHCO}_2\text{CH}_3$	None added UV + peroxide	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (82) $n\text{-C}_3\text{H}_7\text{S}(\text{CH}_2)_3\text{CO}_2\text{CH}_3$ (37) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CO}_2\text{CH}_3)(\text{CH}_2)_3\text{CO}_2\text{CH}_3$ (12) $n\text{-C}_3\text{H}_7\text{S}(\text{CH}_2)_3\text{CH}(\text{CO}_2\text{CH}_3)_2(\text{CH}_2)_3\text{CO}_2\text{CH}_3$ (8) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (40) $n\text{-C}_3\text{H}_7\text{S}(\text{CH}_2)_3\text{CO}_2\text{H}$ (—) $(\text{CH}_2)_3\text{CHSC}(\text{CH}_2)_3\text{C}_6\text{H}_5$ (33)	460 69
$(\text{CH}_3)_2\text{C}(\text{CH}_3)\text{SH}$	$\text{CH}_3=\text{C}(\text{CH}_3)\text{SC}_2\text{H}_4\text{H}_2\text{O}$ $\text{CH}_3=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$ $\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_5$	None added UV FeCl_3	$n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33)	441 456 177, 437, 438 146
$n\text{-C}_3\text{H}_7\text{SH}$	$\text{CH}_3=\text{CHCH}=\text{CH}_2$ $\text{CH}_3\text{CO}_2\text{CH}=\text{CH}_2$	$\text{K}_2\text{S}_2\text{O}_8$ UV	$n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}=\text{CHCH}_3$ + polymer $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (189) $\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (0.6) $\text{H}_2\text{O} + \text{CH}_3\text{CO}_2\text{CH}_3$ (6) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (60) $n\text{-C}_3\text{H}_7\text{S}(\text{CH}_2)_3\text{OC}_2\text{H}_5$ (38) $n\text{-C}_3\text{H}_7\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (72) $n\text{-C}_3\text{H}_7\text{S}(\text{CH}_2)_3\text{OC}_2\text{H}_5$ (94) ^a	76, 110
	$\text{CH}_3=\text{C}(\text{CH}_3)_2$ $\text{CH}_3=\text{CHOC}_2\text{H}_5$ $\text{CH}_3=\text{CHC}_6\text{H}_5$	None added None added X ray Azonitrile None added	$n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (6) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (60) $n\text{-C}_3\text{H}_7\text{S}(\text{CH}_2)_3\text{OC}_2\text{H}_5$ (38) $n\text{-C}_3\text{H}_7\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (33) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (72) $n\text{-C}_3\text{H}_7\text{S}(\text{CH}_2)_3\text{OC}_2\text{H}_5$ (94) ^a	58 442 72, 73 441 442
		Peroxide		438
	$\text{CH}_3=\text{C}(\text{CH}_3)\text{SC}_2\text{H}_4\text{H}_2\text{O}$	Azonitrile	$n\text{-C}_3\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_2)_3\text{SC}_2\text{H}_4\text{H}_2\text{O}$ (85)	441
		None added		451

Note. References 313 to 431 are on pp. 371-376.

^a No structure was given for this product.

^b The product contained 4-5% of the normal adduct, $n\text{-C}_3\text{H}_7\text{SCH}(\text{CH}_2)_3\text{OC}_2\text{H}_5$.

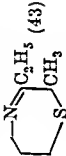

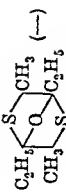



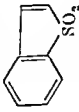
n C_2H_5SH	$3,4$ $CH_3O_2C_2H_4CH_2CH=CH_2$ $3,4$ $CH_3O_2C_2H_4CH=CHCH_2$	Peroxide Peroxide	$3,4$ $CH_3O_2C_2H_4CH_2CH_2SC_2H_4H_{11}^{n-1}$ $3,4$ $CH_3O_2C_2H_4CH_2CH_2SC_2H_4H_{11}^{n-1}$ (—)	436 436
C_2H_5SH (mixed isomers)		None added	$C_2H_5SC_2H_4H_{11}^{n-1}$ (78)	405
4 C_2H_5SH *	 	UV None added	 $1:1$ Adduct/ (—)	108 106
$C_4H_9COCH(CH_3)SH$	$(CH_3)_2C=CH(CH_2)_4C(CH_3)=CHCH_3$ Squalene (dihydrosymonene) $CH_2=CHCl$	None added Peroxide Peroxide + UV	$1:1$ Adduct/ (38) $2:1$ Adduct/ (48) Viscous oil $C_4H_9COCH(CH_3)SC_2H_4CH_2Cl$ (22)	108 108 108 176
	$CH_2=CHCH_2Br$	Peroxide	 (—)	176
	$CH_2=CHCH_2Cl$ $CH_2=CHCH_2OH$	Peroxide Peroxide	$C_4H_9COCH(CH_3)SC_2H_4CH_2Cl$ (20) $C_4H_9COCH(CH_3)SC_2H_4CH_2OH$ (21)	176 176






Note: References 385 to 431 are on pp 371-376

* No structure was given for this product

* This thiol is called "isopentanthiol" in ref 108, but no structure is given




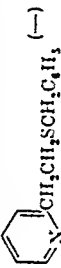
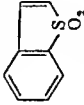
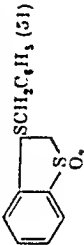
TABLE X—Continued
A. Addition of Aliphatic Thiols to Olefins—Continued



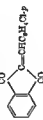

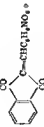

Thiol	Olefin	Catalyst	Products (%)	Refs.
$C_2H_5COCH(CH_3)SH$ (<i>contd.</i>)	$CH_2=CHCH_2NH_2$	Peroxide	 (43)	176
	$CH_3CH=C(CH_3)_2$	Azonitrile	$C_{16}H_{30}N_2S_2$ (23) $C_2H_5COCH(CH_3)SCH(CH_3)CH(CH_3)_2$ (38)	466
		Peroxide or UV	 (—)	176
		Peroxide	$SCH(CH_3)COC_2H_5$ (44)	466
		Peroxide	$SCH(CH_3)COC_2H_5$ (33)	466
$C_4H_9CH=CH_2$		Peroxide	$C_2H_5COCH(CH_3)S(CH_2)_2C_6H_5$ (55)	466
$C_6H_5CH=CHCH_2OH$		Peroxide	 (16)	176
$n-C_{11}H_{23}CH=CH_2 + CO$ (2900–3000 atm.)		Peroxide	$n-C_6H_{13}SCH_2CH(CHO)C_4H_9 \cdot n$ (8)	81, 427
$CH_2=CHB(OC_4H_9)_2$		UV	$n-C_6H_{13}S$ (37)	467
$CH_3=CH(CH_2)_6CO_2H$		UV	$n-C_6H_{13}S(CH_2)_2B(OC_4H_9)_2$ (93) $n-C_6H_{13}S(CH_2)_{10}CO_2H$ (—)	456
		Peroxide	$SC_6H_{13} \cdot n$ (34)	141
$3,4-CH_2O_2C_2H_5CH_2CH=CH_2$		Peroxide	$3,4-CH_2O_2C_2H_5(CH_2)_3SC_6H_{13} \cdot n$ (—)	436
$3,4-CH_2O_2C_2H_5CH=CHCH_3$		Peroxide	$3,4-CH_2O_2C_2H_5CH_2CH(CH_3)SC_6H_{13} \cdot n$ (—)	436

	$\text{CH}_2=\text{CHCH}_2\text{OH}$	Peroxide		464
		UV		468
	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$	Peroxide	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4(\text{CH}_2)_3\text{S} \text{---} \text{Cyclohexane}$	435
$n\text{-C}_6\text{H}_5\text{O}(\text{CH}_2)_5\text{SH}$	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}=\text{CHCH}_2$	Peroxide	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}_2\text{CH}(\text{CH}_2)_5\text{S} \text{---} \text{Cyclohexane}$	436
	$\text{CH}_2=\text{CHOC}_2\text{H}_5$	None added	$n \text{ C}_6\text{H}_5\text{O}(\text{CH}_2)_5\text{S}(\text{CH}_2)_2\text{OC}_2\text{H}_5$	439
	$n \text{ C}_6\text{H}_5\text{SCH}=\text{CH}_2$	None added	$n \text{ C}_6\text{H}_5\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OC}_2\text{H}_5$	442
	$n \text{ C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{SCH}=\text{CH}_2$	None added	$n \text{ C}_6\text{H}_5\text{O}(\text{CH}_2)_5\text{S}(\text{CH}_2)_2\text{SCH}_2\text{CH}_2\text{OC}_2\text{H}_5$	469
	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$	Peroxide	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4(\text{CH}_2)_3\text{SCH}_2\text{CH}_2\text{OC}_2\text{H}_5$	436
	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}=\text{CHCH}_2$	Peroxide	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}_2\text{CH}(\text{CH}_2)_3\text{SCH}_2\text{CH}_2\text{OC}_2\text{H}_5$	436
$\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SH}$	$\text{CH}_2=\text{C}=\text{CH}_2$ 	Azonitrile	1:1 Adduct ---	131
$n\text{-C}_6\text{H}_5\text{CH}_2\text{SH}$ $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SH}$ $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$ $3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$ $2,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}=\text{CHCH}_2$ $\text{CCl}_3\text{CH}=\text{CH}_2$	Peroxide Peroxide Peroxide UV	$3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4(\text{CH}_2)_3\text{SCH}_2\text{C}_6\text{H}_5$ $3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4(\text{CH}_2)_3\text{SCH}_2\text{C}_6\text{H}_4\text{Cl}$ $3,4 \text{ CH}_3\text{O}_2\text{C}_2\text{H}_4\text{CH}(\text{CH}_2)_3\text{SCH}_2\text{C}_6\text{H}_4\text{Cl}$ $\text{CCl}_3\text{CH}(\text{CH}_2)_3\text{SCH}_2\text{C}_6\text{H}_5$	436 436 436 121
	$\text{CH}_2=\text{CHCHO}$ $\text{CH}_2=\text{CHCH}_2\text{OH}$ $\text{CH}_2\text{CH}=\text{CHCHO}$ $\text{CH}_3\text{CO}_2\text{CH}=\text{CH}_2$	None added Peroxide Peroxide UV	$\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{CHO}$ $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$ $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{CHO}$ $\text{CH}_3\text{CO}_2(\text{CH}_2)_3\text{SCH}_2\text{C}_6\text{H}_5$	135 113 113, 135 110

Notes: References 355 to 631 are on pp. 371-376.
 / No structure was given for this product.

TABLE X—Continued
A. Addition of Aliphatic Thiols to Olefins—Continued

Thiol	Olefin	Catalyst	Products (%)	Refs.
$C_6H_5CH_2SH$ (contd.)	$CH_3CH=CHCO_2H$	Peroxide	$C_6H_5CH_2SCH(CH_3)CH_2CO_2H$ (95)	113, 131
	$CH_2=C(CO_2H)CH_2CO_2H$	Azonitrilo	$C_6H_5CH_2SCH_2CH(CO_2H)CH_2CO_2H$ (40)	470
	$CH_3CH=C(CH_3)_2$	None added	$C_6H_5CH_2SCH(CH_3)CH(CH_3)_2$ (—)	63
		Sunlight or peroxide	 (97)	113, 166, 168, 471
	$CH_3CO_2CH_2C(CH_3)=CH_2$	Peroxide	$CH_3CO_2CH_2CH(CH_3)CH_2SCH_2C_6H_5$ (73)	113
	$CH_2=CHSi(CH_3)_2OC_2H_5$	None added	$C_6H_5CH_2S(CH_3)_2Si(CH_3)_2OC_2H_5$ (26)	472
		Peroxide	 (—)	436, 109
	$CH_2=CHSi(CH_3)_2OC_2H_5$	None added	$C_6H_5CH_2S(CH_3)_2Si(CH_3)_2OC_2H_5$ (—)	472
		Peroxide	 (51)	141
	$C_6H_5CH=CH_2$	Peroxide	$C_6H_5CH_2S(CH_3)_2C_6H_5$ (93)	113, 466, 436
	$CH_2=CHSi(OC_2H_5)_3$	None added	$C_6H_5CH_2Si(CH_3)_2Si(OC_2H_5)_2$ (34)	472
	$C_6H_5CH=CHCO_2H$	Peroxide	$C_6H_5CH_2SCH(CH_3)CH_2CO_2H$ (35)	113
	$C_6H_5C(CH_3)=CH_2$	None added	$C_6H_5CH_2SCH_2CH(CH_3)C_6H_5$ (—)	63
	$C_6H_5CH=CHCH_2OH$	Peroxide	$C_6H_5CH_2SCH(CH_3)_2CH_2OH$ (17)	113

	None added		63
$\text{C}_6\text{H}_5\text{COCH}=\text{CHCOOC}_6\text{H}_5$ $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOC}_6\text{H}_5$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_2$ $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5$ $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{H}$ $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOC}_6\text{H}_5$	None added None added Peroxide Peroxide Peroxide UV None added	$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}(\text{CO}_2\text{H})\text{SCH}_2\text{C}_6\text{H}_5$ (—) $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCOC}_6\text{H}_5$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4(\text{CH}_2)_2\text{SCH}_2\text{C}_6\text{H}_5$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5)$ (—) $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{SCH}_2\text{C}_6\text{H}_5$ (3a) $\text{C}_6\text{H}_5\text{CH}_2\text{S}(\text{CH}_2)_3\text{CO}_2\text{H}$ (—) $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCOC}_6\text{H}_5$ (—)	122 123 436 436 113 466 123
	None added		136
	None added		136

Note: References 345 to 631 are on pp. 371-376.

^a No structure was given for this product.



^b The product was isolated as the sulfone.



^c The structure was not proved.

^d The configuration of the product is not known.

^e The product was isolated as the oxime.

TABLE X—Continued
A. Addition of Aliphatic Thiols to Olefins—Continued



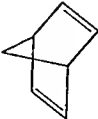



Thiol	Olefin	Catalyst	Products (%)	Refs.
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{SH}$	$\text{C}_6\text{H}_5\text{CH}=\text{CHNO}_2$ $p\text{-O}_2\text{NC}_6\text{H}_4\text{COCH}=\text{CHC}_6\text{H}_5$	Peroxide Peroxide	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{SCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{NO}_2$ (44) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{SCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{-}$ $\text{COC}_6\text{H}_4\text{NO}_2\text{-}p$ (74)	124 124
	$\text{C}_6\text{H}_5\text{COCH}=\text{CHCOC}_6\text{H}_5$ (trans)	Peroxide	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{SCH}(\text{COC}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$ (91)	124
$\text{C}_6\text{H}_5\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{SCH}_2\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{-}$ $\text{CH}(\text{CH}_3)\text{SCH}_2\text{CH}_2\text{OCH}_2\text{C}_6\text{H}_5$ (—)	436 436
$p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{-}$ $\text{CH}(\text{CH}_3)\text{SCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{CH}_3\text{-}p$ (—)	436
 $\text{CH}_2\text{O}(\text{CH}_2)_2\text{-O}(\text{CH}_2)_2\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{-}$ $\text{CH}(\text{CH}_3)\text{S}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OCH}_2\text{-}$  (—)	436
$p\text{-(t-C}_4\text{H}_9\text{)C}_6\text{H}_4\text{CH}_2\text{SH}$ $\text{C}_6\text{H}_5(\text{OCH}_2\text{CH}_2)_2\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide Peroxide Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{SCH}_2\text{C}_6\text{H}_4(\text{C}_4\text{H}_9\text{-})\text{-}p$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{SCH}_2\text{CH}_2\text{O}_2\text{C}_6\text{H}_5$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{S}(\text{CH}_2\text{CH}_2\text{O})_2\text{C}_6\text{H}_5$ (—)	436 436 436
$o\text{-CH}_3\text{OC}_6\text{H}_4\text{O}(\text{CH}_2)_3\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{S}(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{OCH}_3\text{-}o$ (—) $\text{CH}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{OCH}_3\text{-}o$ (—)	436 436
$m\text{-CH}_3\text{OC}_6\text{H}_4\text{O}(\text{CH}_2)_3\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{S}(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{OCH}_3\text{-}m$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{-}$ $\text{CH}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{OCH}_3\text{-}m$ (—)	436 436
$p\text{-CH}_3\text{OC}_6\text{H}_4\text{O}(\text{CH}_2)_3\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{S}(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{OCH}_3\text{-}p$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{-}$ $\text{CH}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{OC}_6\text{H}_4\text{OCH}_3\text{-}p$ (—)	436 436
$n\text{-C}_{10}\text{H}_{21}\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{SC}_{10}\text{H}_{21}\text{-}n$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{SC}_{10}\text{H}_{21}\text{-}n$ (—)	436 436
$n\text{-C}_8\text{H}_{17}\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$	Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3(\text{CH}_2)_3\text{S}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OC}_6\text{H}_5\text{-}n$ (—) $\text{CH}(\text{CH}_3)\text{S}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2\text{OC}_6\text{H}_5\text{-}n$ (—)	436 436
$n\text{-C}_8\text{H}_{17}(\text{OCH}_2\text{CH}_2)_3\text{SH}$	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{CH}=\text{CH}_2$ $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}=\text{CHCH}_3$	Peroxide Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{-}$ $\text{S}(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{OC}_6\text{H}_{13}\text{-}n$ (—) $3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_3\text{CH}_2\text{-}$ $\text{CH}(\text{CH}_3)\text{S}(\text{CH}_2)_3\text{O}(\text{CH}_2)_3\text{OC}_6\text{H}_{13}\text{-}n$ (—)	436 436




n $CH_3OC_2H_5$ ($OC_2H_5CH_2$) $_nSH$	$3,4$ $CH_2O_2C_2H_5CH_2CH=CH_2$	Peroxide	$3,4$ $CH_2O_2C_2H_5CH_2CH=CH_2$ $S(CH_2CH_2O_2C_2H_5CH_2CH=CH_2)_n$ (—)	436
n C_2H_5SH $3CH_3-6+$ $C_2H_5C_2H_5O(CH_2)_4SH$	$3,4$ $CH_2O_2C_2H_5CH=CHCH_3$ $CH_2=CH(CH_2)_4CO_2H$ $3,4$ $CH_2O_2C_2H_5CH_2CH=CH_2$ $3,4$ $CH_2O_2C_2H_5CH=CHCH_3$	Peroxide UV Peroxide	$3,4$ $CH_2O_2C_2H_5CH_2CH=CH_2$ $S(CH_2CH_2O_2C_2H_5CH_2CH=CH_2)_n$ (—) n $C_2H_5SCH_2CH_2CO_2H$ (—) $3,4$ $CH_2O_2C_2H_5CH_2CH_2S(CH_2)_4$ $OC_2H_5CH_2-3$ C_2H_5-5 (—) $3,4$ $CH_2O_2C_2H_5CH_2CH(CH_2)_4S(CH_2)_4-$ $OC_2H_5CH_2-3$ C_2H_5-5 (—) n $C_2H_5SCH_2CH_2Cl$ (99) n $C_2H_5SCH_2CH_2(CO_2C_2H_5)_nH$ $+ (n-C_{10}H_{21})_2S_2$ (34) $n = 1$ (17) $n = 2$ (21) $n = 3$ (16) $n \geq 4$ (13)	436 456 436 436
n C_2H_5SH	$CF_3=CFCF_3$ $CH_2=CHCO_2C_2H_5$	Peroxide + UV Peroxide	$OC_2H_5CH_2-3$ C_2H_5-5 (—) n $C_2H_5SCH_2CH_2(CO_2C_2H_5)_nH$ $+ (n-C_{10}H_{21})_2S_2$ (34) $n = 1$ (17) $n = 2$ (21) $n = 3$ (16) $n \geq 4$ (13)	436 119 89
	$(CH_2=CHCH_2)_2O$	UV	n $C_2H_5SCH_2CH_2OC(CH_2)_4CH=CH_2$ (—) n $C_2H_5SCH_2CH_2O(CH_2)_4SC_2H_5$ (—)	474
		$(C_2H_5)_2S_2 + UV$	 $(CH_2)_2SC_2H_5$ (60)	109
	$C_2H_5CH=CH_2$	$(C_2H_5)_2S_2 + UV$	n $C_2H_5SCH_2CH_2C(CH_2)_4H$ (73) $n = 1, 2$, and larger $3,4$ $CH_2O_2C_2H_5CH_2CH_2SC_2H_5$ n (—) $3,4$ $CH_2O_2C_2H_5CH_2CH_2CH(CH_2)_4SC_2H_5$ n (—) n $C_2H_5SCH_2CH_2CO_2H$ (—) n $C_2H_5SCH_2CH_2$ (—) n $C_2H_5SCH_2CH_2$ n (—) n $C_2H_5SCH_2CH_2$ n (—) n $C_2H_5SCH_2CH_2$ n (—) n $C_2H_5SCH_2CH_2$ n (—)	90 436 436 456 67 67 137 67 67 67

Note. References 385 to 631 are on pp. 371-376

TABLE X—Continued

B. Addition of Mercapto Acids to Olefins

Mercapto Acid	Olefin	Catalyst	Products (%)	Refs.
$\text{HSCH}_2\text{CO}_2\text{H}$	$\text{CH}_2=\text{CHCN}$	Peroxide	$\text{NC}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (74)	475
	$\text{CH}_2=\text{CHCO}_2\text{H}$	Peroxide	$\text{HO}_2\text{C}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (69)	475
	$\text{CH}_2=\text{CHCH}_2\text{Cl}$	Peroxide	$\text{HO}_2\text{CCH}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (74)	476
	$\text{CH}_3\text{COCH}=\text{CHCO}_2\text{H}$	None added	$\text{CH}_3\text{COCH}_2\text{CH}(\text{CO}_2\text{H})\text{SCH}_2\text{CO}_2\text{H}$ (52)	477
	$\text{CH}_2=\text{CHCH}_2\text{SCH}_2\text{CO}_2\text{H}$	Peroxide	$\text{HO}_2\text{CCH}_2\text{S}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (70)	478
	$(\text{CH}_3)_2\text{SiCH}=\text{CH}_2$	None added	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (25)	479, 480
		None added	 (83)	406, 468, 108, 481
	$(\text{CH}_3)_3\text{SiCH}_2\text{CH}=\text{CH}_2$	None added	$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (54)	479, 480
		None added	 (—)	482
		Peroxide	 (100)	466, 108
	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	None added	$\text{C}_6\text{H}_5(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (91)	406
	$n\text{-C}_8\text{H}_{17}\text{CH}=\text{CH}_2$	None added	$n\text{-C}_8\text{H}_{17}\text{SCH}_2\text{CO}_2\text{H}$ (95)	483
	$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2\text{CH}_2\text{CH}=\text{CH}_2$	None added	$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (46)	479, 480
	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{CH}=\text{CH}_2$	None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$ (—)	447
	$n\text{-C}_7\text{H}_{15}\text{CH}=\text{CH}_2$	None added	$n\text{-C}_7\text{H}_{15}\text{SCH}_2\text{CO}_2\text{H}$ (95)	483

$C_4H_7COCH=CHCO_2H$ $3,4\ CH_2O_2C_4H_7CH_2CH=CH_2$ $3,4\ CH_2O_2C_4H_7CH=CHCH_2$						122 426 426
						
$p\text{-}CH_3OC_6H_4CH=CHCH_3$  $CH_3C=CH_2$ (Dipentene)  $CH_3C=CH_2$ (+ Limonene)	None added ^a Peroxide Peroxide					
	None added	1,1 added ^c (78)				463
	Peroxide + UV	$C_{10}H_{16}O_2$ 5' (90)				476
	UV	$C_{10}H_{16}O_2$ 3' (80)				476
	Peroxide	$C_{10}H_{16}O_2$ 3' (86) or $C_{10}H_{16}O_2$ 3' (85)				476

Note. References 385 to 631 are on pp 371-376

^f No structure was given for this product

[†] The configuration of this product was not given.

^a The reactants were dissolved in aqueous sodium bicarbonate.

TABLE X—Continued
B. Addition of Mercapto Acids to Olefins—Continued






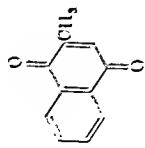
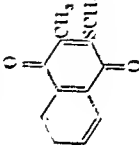







Mercapto Acid	Olefin	Catalyst	Products (%)	Refs.
$\text{HSCH}_2\text{CO}_2\text{H}$ (contd.)	 $\text{CH}_3\text{C}=\text{CH}_2$ (—-Limonene)	Peroxide	$\text{C}_{11}\text{H}_{21}\text{O}_2\text{S}'$ (80)	476
	 (α-Pinene)	UV	$\text{C}_{12}\text{H}_{20}\text{O}_2\text{S}'$ (63)	476
	 (β-Pinene)	Peroxide	$\text{C}_{12}\text{H}_{20}\text{O}_2\text{S}'$ (82)	476

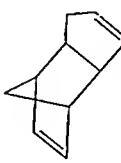



TABLE X—Continued
B. Addition of Mercapto Acids to Olefins—Continued

Mercapto Acid	Olefin	Catalyst	Products (%)	Refs.
$\text{HSCH}_2\text{CO}_2\text{H}$ (contd.)	$n\text{-C}_4\text{H}_9\text{CHOHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CO}_2\text{H}$	Air	$n\text{-C}_4\text{H}_9\text{CHOH}(\text{CH}_2)_{102}$ $\text{CH}(\text{SCH}_2\text{CO}_2\text{H})(\text{CH}_2)_{87}\text{CO}_2\text{H}$ (—)	180
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}_2$	None added	$\text{C}_{21}\text{H}_{33}\text{O}_4\text{S}^2$ (two isomers) (40)	486
	$\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{CH}_3$ (Methyl linoleate)	Peroxide	$\text{CH}_3(\text{CH}_2)_{87}\text{CH}(\text{SCH}_2\text{CO}_2\text{H})(\text{CH}_2)_{150}\text{CO}_2\text{CH}_3$ (—)	485
	$n\text{-C}_4\text{H}_9\text{CHOHCH}_2\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_4\text{H}_9\text{CHOH}(\text{CH}_2)_{102}$ $\text{CH}(\text{SCH}_2\text{CO}_2\text{H})(\text{CH}_2)_{87}\text{CO}_2\text{CH}_3$ (89)	485
	$\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{CH}_3$ (Methyl ricinoleate)	Air	2:1 Adduct ¹ (100)	180
$\text{HSCH}_2\text{CO}_2\text{C}_2\text{H}_5$	$\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_2\text{H}_5$ (Ethyl linoleate)	Air	Triadduct ¹ (100)	180
	Ricinoleic acid triglyceride $(\text{CH}_2)_2\text{Si}(\text{CH}_2)_7\text{CH}=\text{CH}_2$	None added	$(\text{CH}_2)_2\text{Si}(\text{CH}_2)_8\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$ (63)	479, 480
	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	None added	$\text{C}_6\text{H}_5(\text{CH}_2)_8\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$ (—)	114
	$(\text{C}_2\text{H}_5\text{O})_3\text{SiCH}_2\text{CH}=\text{CH}_2$	None added	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_8\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$ (48)	479, 487 ^a
	$(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_2)_7\text{CH}=\text{CH}_2$	Peroxide	$(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_2)_8\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$ (86)	488
$\text{HSCH}_2\text{CH}=\text{CH}_2$	$n\text{-C}_4\text{H}_9\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}_2$ (Ethyl linoleate)	Air	2:1 Adduct ¹ (100)	489
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_2\text{H}_5$	Peroxide	$\text{CH}_3(\text{CH}_2)_{87}\text{CH}(\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5)\text{CH}(\text{CH}_2)_{150}\text{CO}_2\text{C}_2\text{H}_5$ (—)	180
		UV	 (75)	468
	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	None added	$\text{C}_6\text{H}_5(\text{CH}_2)_8\text{SCH}_2\text{CH}_2\text{CO}_2\text{H}$ (—)	490
		None added	 (30)	491

$\text{HSCl}_2(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$	$\text{CH}_2\text{CH}=\text{CH}_2$ HCCO_2H HCCO_2H	Peroxide	$\text{Cl}(\text{CH}_2)_3\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (35)	492
		None added	$\text{HO}_2\text{CCH}_2\text{CH}(\text{CO}_2\text{H})\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (43)	493
		Peroxide	 $\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (75)	492
	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	Peroxide	$n\text{-C}_6\text{H}_{13}\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (85)	492
		Peroxide	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (85)	492
		Peroxide	$(\text{CH}_3)_2\text{CCH}(\text{CH}_3)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (75)	492
		Peroxide or UV	 $\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (83)	492, 493
	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ $(\text{CH}_3)_2\text{CCH}(\text{CH}_3)\text{CH}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CHC}_6\text{H}_5$	Peroxide	$n\text{-C}_6\text{H}_{13}\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (100)	492
		Peroxide	$(\text{CH}_3)_2\text{CCH}(\text{CH}_3)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (92)	492
		Peroxide	$(\text{CH}_3)_2\text{CCH}(\text{C}_6\text{H}_5)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (60)	492
		Peroxide	 $\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (73)	492
	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ $(\text{CH}_3)_2\text{CCH}(\text{CH}_3)\text{CH}=\text{CH}_2$ $(\text{C}_6\text{H}_5)_2\text{C}=\text{CHCH}_3$	Peroxide	$n\text{-C}_6\text{H}_{13}\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (89)	492
		Peroxide	$(\text{CH}_3)_2\text{CCH}(\text{CH}_3)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (90)	492
		Peroxide	$(\text{C}_6\text{H}_5)_2\text{CCH}(\text{CH}_3)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (45)	492
	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ $n\text{-C}_6\text{H}_{13}\text{CH}=\text{CHCH}_3$ $n\text{-C}_6\text{H}_{13}\text{C}(\text{C}_6\text{H}_5)=\text{CH}_2$	Peroxide	$n\text{-C}_6\text{H}_{13}\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (96)	492
		Peroxide	$n\text{-C}_6\text{H}_{13}\text{CH}(\text{CH}_3)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (94)	492
		Peroxide	$n\text{-C}_6\text{H}_{13}\text{CH}(\text{C}_6\text{H}_5)\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (81)	492
	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ $n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ $n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_6\text{H}_{13}\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (92)	492
		Peroxide	$n\text{-C}_6\text{H}_{13}\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (76)	492
		Peroxide	$n\text{-C}_6\text{H}_{13}\text{SCH}(\text{CO}_2\text{H})(\text{CH}_2\text{CO}_2\text{H})$ (94)	492
$\text{HSCl}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{OCOC}_2\text{H}_5$	$(\text{CH}_2)_3\text{CH}=\text{CH}_2$ $\text{O}(\text{S})(\text{CH}_2)_3\text{CH}_2\text{CH}=\text{CH}_2$	None added	Polymer (—)	479
		None added	Polymer (—)	479

Note. References 385 to 631 are on pp. 371-376
 / No structure was given for this product.

TABLE X—Continued

C. Addition of Aliphatic Dithiols to Olefins			
Thiol	Olefin	Catalyst	Products (%)
HSCH ₂ CH ₂ SH	CHCl=CH ₂	Phenyl disulfido + UV	Cl(CH ₂) ₂ S(CH ₂) ₂ S(CH ₂)CH (100)
	HOCH ₂ CH=CH ₂	Peroxide + UV	HO(CH ₂) ₂ SCH ₂ CH ₂ S(CH ₂) ₂ OH (56)
	CH ₂ =C=CH ₂	Azonitrile + UV	CH ₂ =CHCH ₂ S(CH ₂) ₂ SCH ₂ CH=CH ₂ O=C—O (39)
	CH ₂ =CHCH=CH ₂	UV	Polymer (mol. wt. = 1100) (40)
	CH ₂ =CH(CH ₂) ₂ CH=CH ₂	UV	(C ₂ H ₄ S ₂) _x
	CH=CH ₂	None added	Polymer (mol. wt. = 1060) (87)
	p-CH ₃ C ₆ H ₄ SCCH=CH ₂	None added	p-CH ₃ C ₆ H ₄ S(CH ₂) ₂ S(CH ₂) ₂ - S(CH ₂) ₂ SC ₆ H ₄ CH ₃ , p (—)
		None added	C ₁₀ H ₁₂ SCH ₂ CH ₂ SC ₁₀ H ₁₂ ' (—)
	CH ₂ =CH(CH ₂) ₃ CO ₂ H n-C ₁₁ H ₂₂ CH=CH ₂	None added Peroxide	HO ₂ C(CH ₂) ₁₀ S(CH ₂) ₂ S(CH ₂) ₁₀ CO ₂ H (60) n-C ₁₁ H ₂₂ S(CH ₂) ₂ SC ₁₁ H ₂₂ , n (—)
		UV	S(CH ₂) ₂ S  (100)
HS(CH ₂) ₃ SH	CH ₂ =CH(CH ₂) ₃ CO ₂ H n-C ₁₁ H ₂₂ CH=CH ₂	None added Peroxide	HO ₂ C(CH ₂) ₁₀ S(CH ₂) ₃ S(CH ₂) ₁₀ CO ₂ H (47) n-C ₁₁ H ₂₂ S(CH ₂) ₃ SC ₁₂ H ₂₂ , n (—)
		None added Peroxide	HO ₂ C(CH ₂) ₁₀ S(CH ₂) ₃ S(CH ₂) ₁₀ CO ₂ H (47) n-C ₁₁ H ₂₂ S(CH ₂) ₃ SC ₁₂ H ₂₂ , n (—)

Thiol

HSCH₂CH₂SHHS(CH₂)₃SH

Olefin

CHCl=CH₂HOCH₂CH=CH₂CH₂=C=CH₂
O=C—OCH₂=CHCH=CH₂
CH₂=CH(CH₂)₂CH=CH₂CH=CH₂
p-CH₃C₆H₄SCCH=CH₂CH₂=CH(CH₂)₃CO₂H
n-C₁₁H₂₂CH=CH₂CH₂=CH(CH₂)₃CO₂H
n-C₁₁H₂₂CH=CH₂

Catalyst

Phenyl disulfido
+ UV

Peroxide + UV

Azonitrile + UV

UV

UV

None added

None added

None added

None added
Peroxide

UV

None added
Peroxide

Refs.

187

494

181

495

148

495

447, 496,
497




465

498
67

499

498





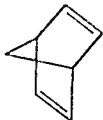
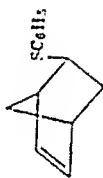
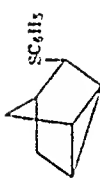
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



$\text{HS}(\text{CH}_2)_7\text{SH}$	$n \text{ C}_{11}\text{H}_{23}\text{CH}=\text{CH}_2$	Peroxide	$n \text{ C}_{11}\text{H}_{22}\text{S}(\text{CH}_2)_7\text{SC}_{11}\text{H}_{22}\text{H}_{27}n (-)$	67
$\text{HS} \left(\begin{array}{c} \text{CH}_2\text{CH}_2\text{SH} \\ \\ \text{H} \end{array} \right)$	$\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{CH}=\text{CH}_2$ 	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{CaSO}_4$	Polymer* (60-65)	118
$\text{HSC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SC}_2\text{H}_4\text{H}$ $\text{OC}_2\text{H}_4\text{SH}$	$\text{CH}_2=\text{CHOC}_2\text{H}_5$ $\text{CH}_2=\text{CHOC}_2\text{H}_5$ n	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{CaSO}_4$	Polymer* (72)	118
$\text{HS}(\text{CH}_2)_7\text{SH}$ $[\text{HS}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7]$	$\text{CH}_2=\text{CHC}_{11}\text{H}_{22}$ n $\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{CH}=\text{CH}_2$	Azonitrile Azonitrile	$\text{C}_7\text{H}_7(\text{OC}_2\text{H}_4\text{SC}_2\text{H}_4\text{OC}_2\text{H}_5)_{11}$ (63) $n \text{ C}_7\text{H}_7(\text{OC}_2\text{H}_4\text{SC}_2\text{H}_4\text{OC}_2\text{H}_5)_n$ (90)	195 195
$\text{HS}(\text{CH}_2)_7\text{SH}$ $[\text{HS}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7]$	$\text{CH}_2=\text{CHC}_{11}\text{H}_{22}$ n $\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{CH}=\text{CH}_2$	Peroxide $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaHSO}_4 + \text{CaSO}_4$	$n \text{ C}_{11}\text{H}_{22}\text{S}(\text{CH}_2)_7\text{SC}_{11}\text{H}_{22}n (-)$ $[(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}]_n$ (57)	67 502
	$(\text{CH}_2=\text{CHCH}_2)_n\text{CHOH}$	UV	$[(\text{CH}_2)_7\text{CHOH}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}]_n$ (60-63)	502
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{N}(\text{CH}_3)_2\text{C}(\text{CH}_3)=\text{CH}_2$	UV	$(\text{CH}_2)_7\text{CH}(\text{CH}_3)(\text{CH}_2)_7\text{CH}(\text{CH}_3)\text{CH}_2$ $\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}$ (81-84)	502
	$(\text{CH}_2)_7\text{S}(\text{CH}_2)_7(\text{CH}_2)_7\text{CH}=\text{CH}_2$	UV	$[(\text{CH}_2)_7\text{S}(\text{CH}_2)_7(\text{CH}_2)_7\text{S}]_n$ (79-85)	502
		UV	$\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S} \\ \\ \text{OH} \end{array} \right]_n$ (77-79)	502
		UV	$\left[\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S}(\text{CH}_2)_7\text{S} \\ \\ \text{OCOCH}_3 \end{array} \right]_n$ (81-84)	502

Note: References 385 to 631 are on pp 371-376

* The structure and empirical formulae were not determined

TABLE X—Continued
D. Addition of Aromatic Thiols to Olefins—Continued

Thiol	Olefin	Catalyst	Products (%)	Refs.
C_6H_5SH (contd.)	$CH_2=CHCH(CH_3)_2$	None added	$C_6H_5S(CH_2)_2CH(CH_3)_2$ (80)	68
		UV	 (49) $(C_6H_5)_2S_2$	92, 97
		UV	 (83)	103, 104
	$CH_2=CHC_6H_5$, ⁿ	Peroxide, + $FeCl_2$	$C_6H_5SC_6H_5$, ⁿ (32)	177, 437, 438
	$CH_2=CHOC_6H_5$, ⁿ	None added	$C_6H_5SCH_2CH_2OC_6H_5$, ⁿ (90-96) $C_6H_5SCH(CH_2)_2OC_6H_5$, ⁿ (3-5)	112
		None added	 (7)	103
			 (23)	

	Peroxide		105, 114, 466
	None added		141
$\text{CH}_2=\text{CHC}_2\text{H}_5$ $\text{CH}_2=\text{CHSO}_2\text{C}_2\text{H}_5$ $\text{CH}_2=\text{CHSO}_2\text{C}_2\text{H}_5$ $\text{CH}_2=\text{CHSO}_2\text{C}_2\text{H}_5$	UV None added None added None added	$\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{C}_2\text{H}_5$ (90) $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (100) $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_2\text{H}_5$ (94) $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_2\text{H}_5$ (75)	64, 63 443 141 472
	None added		461
$\text{CH}_2=\text{CHC}_2\text{H}_5$ $\text{CH}_2=\text{CHSC}_2\text{H}_5$ $\text{CH}_2=\text{CHSC}_2\text{H}_5$ $\text{CH}_2=\text{CHSC}_2\text{H}_5$ $\text{C}_2\text{H}_5\text{COCH}=\text{CHCO}_2\text{H}$ $\text{C}_2\text{H}_5\text{CH}=\text{CHCH}=\text{CH}_2$	None added Aronitrile Aronitrile None added None added	$\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (—) $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (82) $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (82) $\text{C}_2\text{H}_5\text{COCH}_2\text{CHCO}_2\text{H}$ (—) $\text{C}_2\text{H}_5\text{CH}=\text{CHCH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (—)	63 449 448 122 63
	None added		63
$2,4\text{CH}_2\text{O}_2\text{C}_2\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$	Peroxide	$2,4\text{CH}_2\text{O}_2\text{C}_2\text{H}_5(\text{CH}_2)_2\text{SC}_2\text{H}_5$ (—)	436

Note: References 335 to 631 are on pp. 371-376.

* The product was isolated as the sulfone.

TABLE X—Continued
D. Addition of Aromatic Thiols to Olefins—Continued

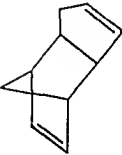
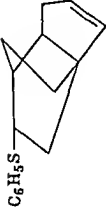
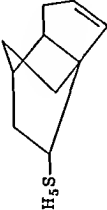


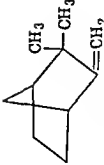
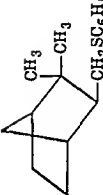
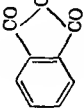

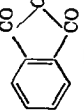

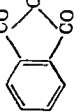

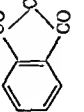

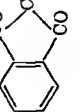

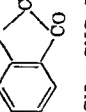









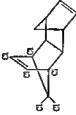
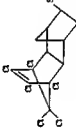


Thiol	Olefin	Catalyst	Products (%)	Refs.
C_6H_5SH (contd.)		None added	<div style="display: flex; align-items: center; justify-content: center;"> <div style="text-align: center;">  <p>C_6H_5S</p> </div> <div style="margin: 0 10px;">or</div> <div style="text-align: center;">  <p>C_6H_5S</p> </div> </div> <p style="text-align: center;">(93)</p>	465
	 $CH_3C=CH_2$ (—Limonene)	None added	 $CH_3CHCH_2SC_6H_5$ (—)	63
	 (Camphene)	None added	 (—)	63

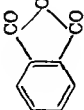
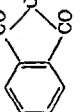
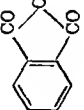
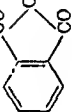
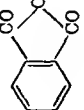
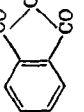
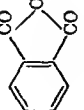
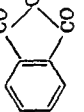
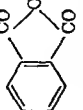
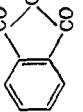
TABLE X—Continued
D. Addition of Aromatic Thiols to Olefins—Continued










Thiol	Olefin	Catalyst	Products (%)	Refs.
C_6H_5SH (contd.)		None added	 $CHCH(SC_6H_5)_2C_6H_4NO_2-o$ (—)	136
		None added	 $CHCH(SC_6H_5)_2C_6H_4NO_2-m$ (—)	136
		None added	 $CHCH(SC_6H_5)_2C_6H_4NO_2-p$ (—)	136
		None added	 $CHCH(C_6H_5)_2SC_6H_5$ (—)	136
		None added	 $CHCH(SC_6H_5)_2C_6H_4CH_3-m$ (—)	136
		None added	 $CHCH(SC_6H_5)_2C_6H_4CH_3-p$ (—)	136
$CH_2=CHC_6H_5$ $CH_2=CHC_6H_5$ Squalone		Peroxide Peroxide Peroxide + UV	$C_6H_5SC_6H_5$ (—) $C_6H_5SC_6H_5$ (—) Nature of product not investigated.	67 67 108

$p\text{-ClC}_6\text{H}_4\text{SH}$		UV		92
		UV		92
		None added		461
	 endo or exo	None added		166
		UV or Peroxide		166
$o\text{-CH}_2\text{C}_6\text{H}_4\text{SH}$		None added		136

Note: References 385 to 631 are on pp. 371-376.

TABLE X—Continued

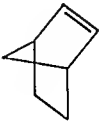
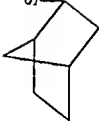
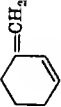

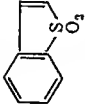



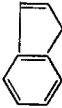
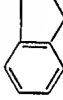
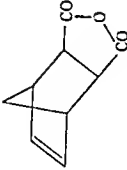
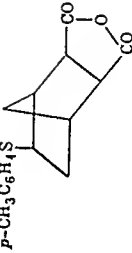
D. Addition of Aromatic Thiols to Olefins—Continued				
Thiol	Olefin	Catalyst	Products (%)	Refs.
<i>o</i> -CH ₃ C ₆ H ₄ SH (contd.)		None added	 CHCH(C ₆ H ₄ NO ₂ - <i>o</i>)SC ₆ H ₄ CH ₃ - <i>o</i> (—)	136
		None added	 CHCH(C ₆ H ₄ NO ₂ - <i>m</i>)SC ₆ H ₄ CH ₃ - <i>o</i> (—)	136
		None added	 CHCH(C ₆ H ₄ NO ₂ - <i>p</i>)SC ₆ H ₄ CH ₃ - <i>o</i> (—)	136
		None added	 CHCH(C ₆ H ₅)SC ₆ H ₄ CH ₃ - <i>o</i> (—)	136
		None added	 CHCH(C ₆ H ₄ CH ₃ - <i>p</i>)SC ₆ H ₄ CH ₃ - <i>o</i> (—)	136
2-CH ₃ -4-ClC ₆ H ₃ SH	CH ₃ =CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i>	None added	2-CH ₃ -4-ClC ₆ H ₃ SCH ₂ CH ₂ SO ₂ C ₆ H ₄ CH ₃ - <i>p</i> (—)	447, 506, 507
<i>m</i> -CH ₃ C ₆ H ₄ SH	CH ₃ =C(CH ₃)CO ₂ CH ₃	UV	<i>m</i> -CH ₃ C ₆ H ₄ SCH ₂ CH(CH ₃)CO ₂ CH ₃ (45) <i>m</i> -CH ₃ C ₆ H ₄ SC(CH ₃)(CO ₂ CH ₃)(CH ₂) ₂ - CH(CH ₃)CO ₂ CH ₃ † (11)	91





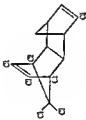
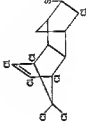
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}$					148 147, 149 447
$\text{CH}_2=\text{CHCH}=\text{CH}_2$ $\text{CH}_2=\text{CHCH}=\text{CH}_2$ $\text{CH}_2=\text{CHSO}_2\text{CH}_3$				$p\text{-CH}_3\text{C}_6\text{H}_4\text{S}(\text{CH}_2)_2\text{SC}_2\text{H}_4\text{CH}_3$, <i>p</i> (38) $p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$ (<i>trans</i>) (90) $p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{SC}_2\text{H}_4$ (—)	
			UV	 $\text{SC}_2\text{H}_4\text{CH}_3$, <i>p</i> <i>trans</i> (—)	92
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$			UV	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$ (78) $p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2(\text{CO}_2\text{CH}_3)_2\text{SCH}_2\text{CH}_3$ $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ (14)	91
$\text{CH}_2=\text{CHC}\equiv\text{CCH}=\text{CH}_2$			UV	$p\text{-CH}_3\text{C}_6\text{H}_4\text{S}(\text{CH}_2)_2\text{C}\equiv\text{C}(\text{CH}_3)_2\text{SC}_2\text{H}_4\text{CH}_3$, <i>p</i> (80)	507a
			UV	 $\text{SC}_2\text{H}_4\text{CH}_3$, <i>p</i> <i>trans</i> (—)	92
$\text{CH}_2=\text{CHCH}_2\text{S}(\text{CH}_2)_3$			None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{S}(\text{CH}_2)_2\text{S}(\text{CH}_2)_3$ (18)	479
			Peroxide	 $\text{CH}_2\text{CH}_2\text{SC}_2\text{H}_4\text{CH}_3$, <i>p</i> (86)	436, 109
			None added	 $\text{SC}_2\text{H}_4\text{CH}_3$, <i>p</i> (89)	101
				 $\text{SC}_2\text{H}_4\text{CH}_3$, <i>p</i> (92)	

Note. References 385 to 631 are on pp. 371-376

* The structure was not proved.

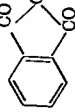
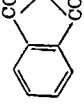
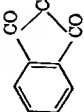
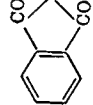
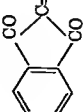
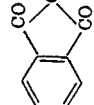
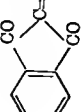
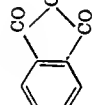
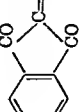
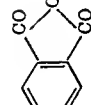
TABLE X—Continued
D. Addition of Aromatic Thiols to Olefins—Continued

Thiol	Olefin	Catalyst	Products (%)	Refs.
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}$ (contd.)		None added	 (86)	100
		None added	 (81)	147
		None added	 (85)	141
		None added	 (88)	147
		None added	 (90)	461
		None added	 $p\text{-CH}_3\text{C}_6\text{H}_4\text{S}$ (73)	101

$\text{CH}_2=\text{CHSC}_6\text{H}_4\text{CH}_3$ <i>p</i>	None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{SC}_6\text{H}_4\text{CH}_3$ <i>p</i> (—)	447, 406, 497
$\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_4\text{CH}_3$ <i>p</i>	None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$ <i>p</i> (—)	447, 506, 507
$\text{C}_6\text{H}_5\text{CH}=\text{CHCOCO}_2\text{H}$	None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCO}_2\text{H}$ (—)	123
$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}=\text{CHCH}_3$	Peroxide	$3,4\text{-CH}_2\text{O}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{SC}_6\text{H}_4\text{CH}_3$ <i>p</i> (—)	436
	None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{S}$ 	101
$\text{CH}_2=\text{CHC}_6\text{H}_4\text{CH}_3$ <i>a</i>	Peroxide	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SC}_6\text{H}_4\text{H}_{12}$ (—)	67
	None added	 $\text{SCH}_2\text{CH}_2\text{SC}_6\text{H}_4\text{CH}_3$ <i>p</i> (—)	447, 406, 497
	None added	 $\text{SC}_6\text{H}_4\text{CH}_3$ <i>p</i> (50)	102

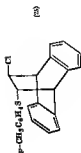
Note: References 355 to 631 are on pp. 371-376.

TABLE X—Continued
D. Addition of Aromatic Thiols to Olefins—Continued

Thiol	Olefin	Catalyst	Products (%)	Refs.
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}$ (contd.)	$\text{CH}_2=\text{CHC}_6\text{H}_{27-n}$	Peroxide	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SC}_6\text{H}_5$ (—)	67
	$\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_4\text{NO}_2$	None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_4\text{NO}_2$ (85)	124
	$\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$	None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$ (—)	123
	$\text{CH}_2=\text{CHC}_6\text{H}_{27-n}$	Peroxide	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SC}_6\text{H}_{27-n}$ (—)	67
		None added	 $\text{CHCH}(\text{C}_6\text{H}_4\text{Cl})\text{SC}_6\text{H}_4\text{CH}_3$ (—)	136
		None added	 $\text{CHCH}(\text{C}_6\text{H}_4\text{NO}_2)$ $\text{SC}_6\text{H}_4\text{CH}_3$ (—)	136
		None added	 $\text{CHCH}(\text{C}_6\text{H}_4\text{NO}_2)$ $\text{SC}_6\text{H}_4\text{CH}_3$ (—)	136
		None added	 $\text{CHCH}(\text{C}_6\text{H}_4\text{NO}_2)$ $\text{SC}_6\text{H}_4\text{CH}_3$ (—)	136
		None added	 $\text{CHCH}(\text{C}_6\text{H}_5)$ $\text{SC}_6\text{H}_4\text{CH}_3$ (—)	136

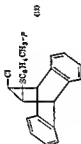


None added

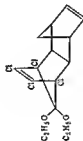


(25)

102



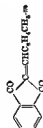
(19)



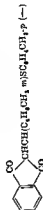
Peroxide



103



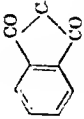



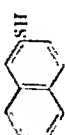
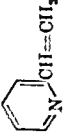
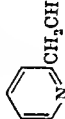
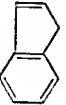

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









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Note: References 383 to 631 are on pp 371-376.


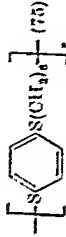

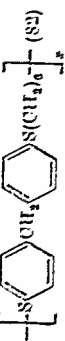
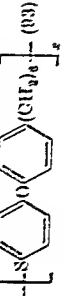
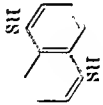
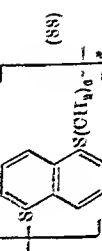
TABLE X—Continued
D. Addition of Aromatic Thiols to Olefins—Continued




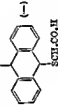

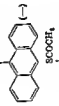
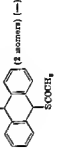
Thiol	Olefin	Catalyst	Products (%)	Refs.
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}$ (contd.)		None added	 $\text{CHCl}(\text{C}_6\text{H}_4\text{CH}_3)_p\text{SC}_6\text{H}_4\text{CH}_3$ (—)	136
	$\text{CH}_3\text{CHClC}_6\text{H}_4\text{H}_n$ $\text{CH}_3\text{CHClC}_6\text{H}_4\text{H}_n$	Peroxide Peroxide	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SC}_{17}\text{H}_{35}$ (—) $p\text{-CH}_3\text{C}_6\text{H}_4\text{SC}_{19}\text{H}_{39}$ (—)	67 67
	$\text{CH}_2=\text{CHSC}_6\text{H}_4$	None added	 $\text{SCH}_2\text{CH}_2\text{SC}_6\text{H}_5$	447, 496, 497
$p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{SH}$	$\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_4\text{H}_n$ $\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_4\text{H}_n$ $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CH}_3$ $n = 5-14$	Peroxide Peroxide Peroxide Peroxide	$p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{SC}_6\text{H}_{13}$ (—) $p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{SC}_6\text{H}_{15}$ (—) $p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{C}_6\text{H}_5$ (—) $p\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{S}(\text{CH}_2)_n\text{CH}_3$ (—) $n = 7-16$	507b 507b 507b 507b
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	UV	$\beta\text{-C}_{10}\text{H}_7\text{SCH}_2\text{CH}(\text{CH}_3)\text{CO}_2\text{CH}_3$ (41) + higher-boiling material	91
		None added	 $\text{CH}_2\text{CH}_2\text{SC}_{10}\text{H}_7$ (41)	109
		None added	 SC_{10}H_7 (91)	401
	$\text{CH}_2=\text{CHSC}_6\text{H}_4\text{CH}_3$	None added	$\beta\text{-C}_{10}\text{H}_7\text{SCH}_2\text{CH}_2\text{SC}_6\text{H}_4\text{CH}_3$ (—)	447, 496
	$\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{H}$	UV	$\beta\text{-C}_{10}\text{H}_7\text{S}(\text{CH}_2)_n\text{CO}_2\text{H}$ (—)	456
	$\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CH}_3$ $n = 8, 10, 12, 14, 16$	Peroxide	$\beta\text{-C}_{10}\text{H}_7\text{S}(\text{CH}_2)_n\text{CH}_3$ (—) $n = 10, 12, 14, 16, 18$	67

	$\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_4\text{CH}_3, p$	None added	 $\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3, p$ (—)	447, 506, 507
	$\text{CH}_2=\text{CHSC}_6\text{H}_4\text{CH}_3, p$	None added	 $\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3, p$ (—)	447, 506, 496, 497
	$\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_4\text{CH}_3, p$	None added	 $\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3, p$ (—)	447
	$\text{CH}_2=\text{CHSC}_6\text{H}_4\text{CH}_3, p$	None added	 $\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3, p$ (—)	447, 496, 506, 497
	$\text{CH}_2=\text{CHSO}_2\text{C}_6\text{H}_4\text{CH}_3, p$	None added	 $\text{SCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3, p$ (—)	447

Note. References 285 to 331 are on pp. 371-376

TABLE X—Continued

<i>E. Addition of Aromatic Dithiols to Olefins</i>				Refs.
Thiol	Olefin	Catalyst	Products (%)	
<i>m</i> -HSC ₆ H ₄ SH	CH ₂ =CHCH=CH ₂	UV	Polymer ^a (75)	495
	CH ₂ =CH(OCH ₂) ₄ OCH=CH ₂	UV	Polymer ^a (—)	495
		UV	Polymer ^a (—)	495
<i>p</i> -HSC ₆ H ₄ SH	CH ₂ =CH(CH ₂) ₃ CH=CH ₂	(NH ₄) ₂ S ₂ O ₈ , NaHSO ₃ + CuSO ₄	 (75)	162
(<i>p</i> -HSC ₄ H ₄) ₂	CH ₂ =CH(CH ₂) ₃ CH=CH ₂	(NH ₄) ₂ S ₂ O ₈ , NaHSO ₃ + CuSO ₄	 (73)	162
(<i>p</i> -HSC ₄ H ₄) ₂ CH ₃	CH ₂ =CH(CH ₂) ₃ CH=CH ₂	(NH ₄) ₂ S ₂ O ₈ , NaHSO ₃ + CuSO ₄	 (82)	152
(<i>p</i> -HSC ₄ H ₄) ₂ O	CH ₂ =CH(CH ₂) ₃ CH=CH ₂	(NH ₄) ₂ S ₂ O ₈ , NaHSO ₃ + CuSO ₄	 (93)	152
	CH ₂ =CH(CH ₂) ₃ CH=CH ₂	(NH ₄) ₂ S ₂ O ₈ , NaHSO ₃ + CuSO ₄	 (88)	152

	$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}=\text{CH}_2$	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{CuSO}_4$	$\left[\text{S} \begin{array}{c} \diagup \text{S}(\text{CH}_2)_6 \diagdown \end{array} \right]_n$ (78)	152
	$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$	$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{CuSO}_4$	$\left[\text{S} \begin{array}{c} \diagup \text{S}(\text{CH}_2)_8 \diagdown \end{array} \right]_n$ (85)	152
$\text{HSCH}_2\text{CO}_2\text{H}$	 + O_2	None added	 (—)	159
CH_3COSE	 + O_2	None added	 (—)	159, 167
			 (2 isomers) (—)	
			$(9 \text{ C}_{14}\text{H}_9)_2\text{S}_2$ (—)	

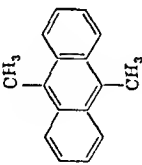
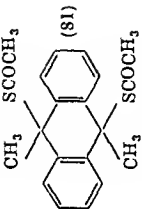
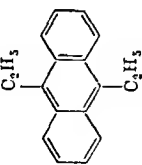
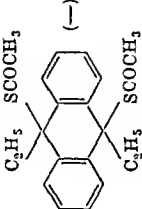


F. Oxidative Addition of Thiols to Olefins



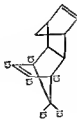
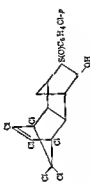


Note. References 355 to 631 are on pp. 371-376

* The structure and empirical formula were not determined.

TABLE X—Continued

F. Oxidative Addition of Thiols to Olefins—Continued

Thiol	Olefin	Catalyst	Products (%)	Refs.
$\text{CH}_3\text{COSiH (contd.)}$		O_2	 (81)	167
$n\text{-C}_3\text{H}_7\text{SH}$		O_2	 (—)	167
$n\text{-C}_3\text{H}_7\text{SH}$	$\text{CH}_2=\text{CHC}_6\text{H}_{13-n} + \text{O}_2$	None added	$n\text{-C}_3\text{H}_7\text{S(O)CH}_2\text{CHOHC}_6\text{H}_{13-n}$ (27) $n\text{-C}_3\text{H}_7\text{SC}_6\text{H}_{17-n}$ (6) $n\text{-C}_3\text{H}_7\text{SCH}_2\text{CHOHC}_6\text{H}_{13-n}$ (5) $n\text{-C}_3\text{H}_7\text{S(O)CH}_2\text{CHOHC}_6\text{H}_5$ (87) $n\text{-C}_3\text{H}_7\text{S(O)CH}_2\text{CH}_2\text{C}_6\text{H}_5$ (1)	111
$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{O}_2$		None added	$(n\text{-C}_3\text{H}_7)_2\text{S}_2$ (1) $(\text{CH}_3)_2\text{CHCH}_2\text{SC}_6\text{H}_5$ (14) $(\text{CH}_3)_2\text{CHCH}_2\text{SO}_2\text{C}_6\text{H}_{13-n}$ (19) $(\text{CH}_3)_2\text{CHCH}_2\text{SCH}_2\text{CHOHC}_4\text{H}_9-n$ (42)	111
$(\text{CH}_3)_3\text{CHCHIL}_2\text{SH}$	$\text{CH}_2=\text{CHC}_6\text{H}_5 + \text{O}_2$	Di- <i>t</i> -butyl diperoxalate	$\text{C}_6\text{H}_5\text{CHOHCCH}_2\text{S(O)C(CH}_3)_3$ (28) $\text{C}_6\text{H}_5(\text{CH}_2)_2\text{SC(CH}_3)_3$ (10) $\text{C}_6\text{H}_5\text{CHO}$ (19)	165, 508
$(\text{CH}_3)_3\text{CSiH}$	$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{O}_2$	α -Cumyl hydroperoxide + FeSO_4	$\text{C}_6\text{H}_5\text{CHOHCCH}_2\text{S(O)C(CH}_3)_3$ (36)	111
	$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{O}_2$	Dibutylamino hydrochloride	$\text{C}_6\text{H}_5\text{CHOHCCH}_2\text{S(O)C(CH}_3)_3$ (36)	162
$p\text{-ClC}_6\text{H}_4\text{SH}$	$\text{C}_6\text{H}_5\text{CH=CH}_2 + \text{O}_2$	None added	$\text{C}_6\text{H}_5\text{CHOHCCH}_2\text{S(O)C(CH}_3)_3$ (—)	159
	 + O_2	None added	 (—)	159

$C_4H_6C(CH_3)=CH_2 + O_3$	None added	$p\text{-ClC}_6H_4S(O)CH_2C(CH_3)(OH)C_2H_5$ $p\text{-ClC}_6H_4SCH_2C(CH_3)(OOH)C_2H_5$ (64)	169
 + O ₃	None added	$p\text{-ClC}_6H_4SO$  HO (11-50)	166
 + O ₃	None added	 (59)	166
$CH_2=CHCN + O_3$	Dibutylamine hydrochloride	$C_4H_9S(O)CH_2CHOHCN$ (20)	162
$CH_2=C(CH_3)CO_2CH_3 + O_3$	Dibutylamine hydrochloride	$C_6H_5S(O)CH_2COH(CH_3)CO_2CH_3$ (—)	162, 163
 + O ₃	Dibutylamine hydrochloride	 (9)	162
$C_4H_6CH=CH_2 + O_3$	None added	$C_4H_9S(O)CH_2CHOHC_2H_5$ (30) $C_4H_9SCH_2CH(OOH)C_2H_5$ (30)	159
$C_4H_6CH=CH_2 + O_3$	Dibutylamine hydrochloride	$C_6H_5S(O)CH_2CHOHC_2H_5$ (23)	162

Note. References 355 to 631 are on pp. 371-376.

TABLE X—Continued
F. Oxidative Addition of Thiols to Olefins—Continued


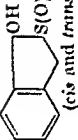
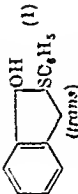



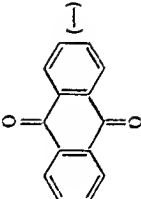
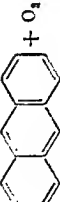
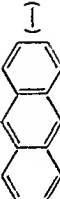



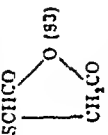
Thiol	Olefin	Catalyst	Products (%)	Refs.
C_6H_5SH (cont'd.)	 + O_2	None added	 (85) (<i>cis</i> and <i>trans</i>)	157, 159
	$C_6H_5C(CH_3)=CH_2 + O_3$	None added	 (1) (<i>trans</i>)	
	 + O_3	None added	$C_6H_5S(O)CH_2C(CH_3)(OH)C_6H_5$ $C_6H_5SCH_2C(CH_3)(OOH)C_6H_5$ (52)	159
	 + O_3	Peroxide + $FeSO_4$	$(C_6H_5)_2S_2$ (—)  (—)	169
			 (—)	
C_6H_5COSH	 + O_2	Peroxide + $FeSO_4$	$SCOC_6H_5$  (—)	169

TABLE X—Continued

F. Oxidative Addition of Thiols to Olefins—Continued






F. Oxidative Addition of Thiols to Olefins—Continued				
Thiol	Olefin	Catalyst	Products (%)	Refs.
$n\text{-C}_{13}\text{H}_{27}\text{SH}$	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2 + \text{O}_2$	UV	$n\text{-C}_{13}\text{H}_{27}\text{S(O)CH}_2\text{CHOHC}_6\text{H}_5$ (75) (two isomers)	159
	 + O_2	UV	 (31)	159
	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2 + \text{O}_2$	UV	$n\text{-C}_{13}\text{H}_{27}\text{S(O)CH}_2\text{C}(\text{CH}_3)(\text{OH})\text{C}_6\text{H}_5$ (10)	159
G. Addition of Thiol Acids to Olefins				
Thiol Acid	Olefin	Catalyst	Products (%)	Refs.
Monobasic CH_3COSH	$\text{CH}_2=\text{CHCl}$ $\text{CH}_2=\text{CHF}$	Air $(n\text{-C}_4\text{H}_9)_2\text{S}_2$ + UV	$\text{CH}_3\text{COSCH}_2\text{CH}_2\text{Cl}$ (51) $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{F}$ (75)	173 186
	$\text{CH}_2=\text{CBzCO}_2\text{H}$ $\text{CH}_2=\text{CClCO}_2\text{H}$ $\text{CH}_2=\text{CHCHO}$ $\text{CH}_2=\text{CHCO}_2\text{H}$ $\text{CH}_2=\text{CHCH}_2\text{Cl}$ $\text{CH}_2=\text{CClCH}_2$ $\text{CH}_2=\text{CHCH}_2$ $\text{CH}_2=\text{CHCH}_2\text{OH}$	None added None added Peroxide None added None added None added UV None added Peroxide	$\text{CH}_3\text{COSCH}_2\text{CHBrCO}_2\text{H}$ (67) $\text{CH}_3\text{COSCH}_2\text{CHClCO}_2\text{H}$ (91) $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{CHO}$ (95) $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{CO}_2\text{H}$ (72) $\text{CH}_3\text{COS}(\text{CH}_2)_3\text{Cl}$ (79) $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{CH}_2$ (94) Unidentified mixture $\text{CH}_3\text{COS}(\text{CH}_2)_3\text{OH}$ (97)	125 509, 125 144, 124 126 310 114, 311 84 144
		Peroxide	 (93)	144, 120
	HCCO_2H HCCO_2H	None added	$\text{CH}_3\text{COSCHCO}_2\text{H}$ $\text{CH}_3\text{CO}_2\text{H}$ (83)	126




$\text{CH}_2=\text{C}(\text{CO}_2\text{H})\text{CH}_2$	UV	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{CO}_2\text{H})\text{CH}_2$ (84)	609, 512
$\text{CH}_2\text{CH}=\text{CHCHO}$	Peroxide	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CH}_2\text{CHO})\text{CH}_2$ (100)	128, 144
$\text{CH}_2\text{COSCH}=\text{CH}_2$	Peroxide	$\text{CH}_2\text{COSCH}_2\text{CH}_2\text{SCoCH}_2$ (53)	178
$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	None added	$\text{CH}_2\text{COSCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ (87)	139
$\text{CH}_2=\text{CHCH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COS}(\text{CH}_2)_2\text{CO}_2\text{H}$ (85)	126
$\text{CH}_2=\text{CHCH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{CH}_2$ (98)	126
$\text{CH}_2\text{CH}=\text{CHCO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2$ (75)	513
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{SCoCH}_2$ (100)	178
$\text{CH}_2\text{CO}_2\text{CH}=\text{CH}_2$	Air	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CHCHCH}_2)$ (57)	25
$\text{CH}_2\text{CH}=\text{CClCH}_2$ (trans)	UV	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CHCHCH}_2)$ (58)	25
$\text{CH}_2\text{CH}=\text{CClCH}_2$ (cis)	UV	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CHCHCH}_2)$ (59)	114, 511
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$	UV	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{Cl})\text{CH}_2$ (88)	68
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	None added	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{CH}_2)_2$ (80)	144
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$	Peroxide	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{OH})\text{CH}_2$ (77)	144
$\text{CH}_2\text{CH}=\text{CHCH}_2\text{OH}$	Peroxide	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})\text{CH}_2$ (55)	126
$\text{CH}_2=\text{C}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CH}_2)_2\text{OCOCH}_2$ (15)	126
CHCO_2H	None added	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ (—)	126
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCHCO}_2\text{H}$ (—)	127
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{NHCOCH}_2\text{CO}_2\text{H})\text{CH}_2$ (83)	516, 516
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}_2\text{CH}(\text{CH}_2\text{CH}_2\text{SCoCH}_2)$ (100)	148
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}_2\text{CH}_2\text{CH}_2\text{CHO}$ (33)	128
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{CH}_2$ (85)	129
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}(\text{CH}_2\text{CH}_2\text{CO}_2\text{H})\text{CH}_2$ (86)	129
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}_2\text{CH}_2\text{CO}_2\text{H}$ (96)	129
$\text{CH}_2\text{CO}_2\text{H}$	None added	$\text{CH}_2\text{COSCH}(\text{CH}_2)_2\text{CH}_2\text{CO}_2\text{H}$ (14)	130

Note: References 385 to 631 are on pp. 371-375.

† The structure was not proved.

TABLE X—Continued
G. Addition of Thiol Acids to Olefins—Continued

Thiol Acid	Olefin	Catalyst	Products (%)	Refs.
Monobasic (contd.)				
CH ₃ COSH (contd.)				
	CH ₃ CO ₂ CH ₂ CH=CH ₂	Peroxide	CH ₃ CO ₂ (CH ₂) ₂ SCoCH ₃ (100)	144
	CH ₃ OCH ₂ CH=CHCO ₂ H	None added	CH ₃ OCH ₂ CH(SCOCH ₃)CH ₂ CO ₂ H (85)	131
	CH ₂ =CH(CH ₂) ₂ Cl	UV	CH ₃ COS(CH ₂) ₂ Cl (87)	114, 511
	CH ₂ CH=CHC ₂ H ₅ (cis and trans)	UV	CH ₃ COSCH(CH ₂)C ₂ H ₄ ⁿ } (98)	114
	CH ₂ =C(CH ₃)C ₂ H ₅	UV	CH ₃ COSCH(C ₂ H ₅) ₂	114
	CH ₂ CH=C(CH ₃)C ₂ H ₅	None added	CH ₃ COSCH(CH ₂)CH(CH ₃)C ₂ H ₅ (52)	88, 406
	CH ₂ =CHCH(CH ₃) ₂	None added	CH ₃ COSCH(CH ₃)CH(CH ₃) ₂ (87)	98
	CH ₂ =CHSCH(CH ₃) ₂	None added	CH ₃ COSCH ₂ CH ₂ CH(CH ₃) ₂ (80)	445
	CH ₂ =CHSCH(CH ₃) ₂	None added	CH ₃ COSCH ₂ CH ₂ Si(CH ₃) ₂ (67)	517
	CH ₂ =CHCH ₂ CH(CO ₂ H) ₂	None added	CH ₃ COS(CH ₂) ₂ CH(CO ₂ H) ₂ (59)	
		UV	 (29% trans) (81)	97, 518
		None added or UV	SCoCH ₃ (100)	114, 112, 384, 408
		UV	 (cis and trans) (80)	98, 114
	CH ₂ =CH(CH ₂) ₂ CH=CH ₂	None added	CH ₃ COS(CH ₂) ₂ SCoCH ₃ (92)	499, 519
	CH ₂ =C(CH ₃)C(CH ₃)=CH ₂	None added	CH ₃ COSCH ₂ C(CH ₃)=C(CH ₃) ₂ or CH ₃ COSCH ₂ CH(CH ₃)C(CH ₃)=CH ₂ (89)	510
	CH ₂ =CHCH ₂ CH ₂ COCH ₃	UV	CH ₃ COS(CH ₂) ₂ COCH ₃ (91)	518, 520
	(CH ₃) ₂ C=CHCOCH ₃	Peroxide	CH ₃ COS(CH ₂) ₂ CH ₂ COCH ₃ (92)	521, 141
	CH ₂ CO ₂ CH ₂ CH=CHCH ₃	Peroxide	CH ₃ CO ₂ CH ₂ CH ₂ CH(CH ₃)SCoCH ₃ (71)	144
	CH ₂ CO ₂ CH ₂ CH=CHC ₂ H ₅	None added	CH ₃ CO ₂ CH ₂ CH ₂ CH(C ₂ H ₅)SCoCH ₃ (72)	99
	CH ₂ CO ₂ CH ₂ C(CH ₃)=CH ₂	Peroxide	CH ₃ CO ₂ CH ₂ CH(CH ₃)CH ₂ SCoCH ₃ (80)	144







$\text{CH}_3\text{CO}_2\text{C}(\text{CH}_3)=\text{CHCH}_3$	None added	$\text{CH}_3\text{CO}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SOCH}_3$ (75)	99
$\text{C}_2\text{H}_5\text{CH}=\text{CHCH}_2\text{CO}_2\text{H}$	Peroxide	$\text{C}_2\text{H}_5\text{CH}(\text{SOCH}_3)\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ (—)	517
$\text{CH}_2=\text{C}(\text{CO}_2\text{H})\text{CH}(\text{CH}_3)_2$	None added	$\text{CH}_3\text{COSCH}_2\text{CH}(\text{CO}_2\text{H})\text{CH}(\text{CH}_3)_2$ (—)	132
$\text{CH}_2=\text{CHC}_2\text{H}_5$ n	UV	$\text{CH}_2\text{COSC}_2\text{H}_5$ n (83)	98, 114
$\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3)_2$	UV	$\text{CH}_2\text{COSC}(\text{CH}_3)_2\text{CH}(\text{CH}_3)_2$ (94)	114
$\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3)_2$	UV	$\text{CH}_2\text{COSC}(\text{C}_2\text{H}_5)_2\text{CH}(\text{CH}_3)_2$ (93)	114
$\text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH}_3)_2$	UV	$\text{CH}_2\text{COSC}(\text{CH}_3)_2\text{CH}(\text{CH}_3)_2$ (94)	114, 384
$\text{CH}_2=\text{CHCH}_2\text{C}_2\text{H}_5$ n	UV	$\text{CH}_2\text{COSC}(\text{CH}_3)_2\text{CH}(\text{C}_2\text{H}_5)_2$ (98)	114, 384
$\text{C}_2\text{H}_5\text{CH}=\text{C}(\text{CH}_3)_2$	UV	$\text{CH}_2\text{COSC}(\text{C}_2\text{H}_5)_2\text{CH}(\text{CH}_3)_2$ (96)	430
$\text{CH}_2=\text{CHOC}_2\text{H}_5$ n	None added	$\text{CH}_2\text{COSC}(\text{CH}_2\text{OC}_2\text{H}_5)_2$ (91)	519
$\text{CH}_2=\text{CHOC}_2\text{H}_5$ n	None added	$\text{CH}_2\text{COSC}(\text{CH}_2\text{OC}_2\text{H}_5)_2$ (92)	445
$\text{CH}_2=\text{CHOC}_2\text{H}_5$ n	None added	$\text{CH}_2\text{COSC}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2$ (79)	174
$\text{CH}_2=\text{CHCH}_2\text{Si}(\text{CH}_3)_2$	None added + UV	$\text{CH}_2\text{COSC}(\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{OCOCCH}_3)$ (31)	522
$\text{CH}_2\text{COSC}(\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{OCOCCH}_3)$	None added	$\text{CH}_2\text{COSC}(\text{CH}_2)_2\text{CH}_2\text{NHCOCH}_3\text{CO}_2\text{H}$ (—)	98, 114, 112
$(\text{CH}_3)_2\text{C}=\text{C}(\text{NHCOCH}_3)\text{CO}_2\text{H}$	UV	 (85) (cis and trans)	
	None added	 (91)	523
$(\text{CH}_3)_2\text{C}=\text{C}(\text{NO}_2)\text{CO}_2\text{C}_2\text{H}_5$	None added	$\text{CH}_2\text{COSC}(\text{CH}_3)_2\text{CH}(\text{NO}_2)\text{CO}_2\text{C}_2\text{H}_5$ (72)	130
$\text{CH}_2=\text{CHCH}_2\text{CH}(\text{CH}_3)\text{COCH}_3$	UV	$\text{CH}_2\text{COSC}(\text{CH}_3)_2\text{CH}(\text{CH}_3)\text{COCH}_3$ (78)	520
$\text{CH}_2=\text{CHCH}_2\text{Si}(\text{CH}_3)_2\text{C}_2\text{H}_5$	None added	$\text{CH}_2\text{COSC}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{C}_2\text{H}_5$ (80)	445
$\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$	None added	$\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{SOCH}_3$ (71)	90, 524
$\text{CH}_2\text{CH}=\text{CHSi}(\text{CH}_3)_2\text{C}_2\text{H}_5$	None added	$\text{CH}_2\text{COSC}(\text{CH}_3)_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{C}_2\text{H}_5$ (58)	445


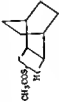

Note. References 385 to 631 are on pp. 371-376.

* The structure was not proved

† The isomers were formed in about equal quantities.

TABLE X—Continued
G. Addition of Thiol Acids to Olefins—Continued

Thiol Acid	Olefin	Catalyst	Products (%)	Refs.
Monobasic (contd.)				
CH ₃ COSH (contd.)		None added	CH ₃ COS—  CH=CH ₂ ^a (18)	118
			 CH ₂ CH ₂ SCOCH ₃ (26)	
			CH ₃ COS—  CH ₂ CH ₂ SCOCH ₃ ^a (36)	
		None added	 OCOCH ₃ (74)	99
	CHCO ₂ C ₂ H ₅ =CHCO ₂ C ₂ H ₅	None added	C ₂ H ₅ OCOCH(SCOCH ₃)CH ₂ CO ₂ C ₂ H ₅ (75)	139
	(CH ₃) ₂ C=CH(CH ₂) ₃ COCH ₃ n-C ₃ H ₇ CH=C(CH ₃)C ₂ H ₅ (CH ₃) ₂ C=CH(CH ₂) ₃ COCH ₃ CH ₃ COSCH=CHC ₄ H ₉ ⁿ CH ₂ =CHC ₆ H ₁₃ ⁿ CH ₃ CH=CHC ₆ H ₁₁ ⁿ	Peroxide None added None added None added Peroxide Peroxide	(CH ₃) ₂ CHCH(SCOCH ₃)(CH ₂) ₂ COCH ₃ (—) C ₁₀ H ₁₈ O ₂ S ^a (52) (CH ₃) ₂ CHCH(SCOCH ₃)(CH ₂) ₂ COCH ₃ (77) CH ₃ COSCH ₂ CH(SCOCH ₃)C ₄ H ₉ ⁿ (60) CH ₃ COSC ₆ H ₁₁ ⁿ (100) CH ₃ COSCH(CH ₃)C ₆ H ₁₃ ⁿ (100) CH ₃ COSCH(C ₂ H ₅)C ₆ H ₁₁ ⁿ (100) CH ₃ COSCH ₂ CH(CH ₃)CH ₂ C(CH ₃) ₃ (87) + other isomers	525 521 520 171 144, 526 144
	Diisobutylene [CH ₃ =C(CH ₃)CH ₂ - C(CH ₃) ₂ -(CH ₂) ₂ C=CHC(CH ₃) ₃ 4:1] CH ₂ =CHCH ₂ CH(OC ₂ H ₅) ₂ (CH ₂ =CHCH ₂) ₂ Si(CH ₃) ₂ CH ₂ =CHCH ₂ Si(CH ₃) ₂ C ₃ H ₇ ⁿ	None added UV None added None added	CH ₃ COS(CH ₂) ₂ CH(OC ₂ H ₅) ₂ (52) [CH ₂ COS(CH ₂) ₂ Si(CH ₃) ₂] ₂ (79) CH ₃ COS(CH ₂) ₂ Si(CH ₃) ₂ C ₃ H ₇ ⁿ (76)	518, 520 502 415

445					
144					
126					
144, 384					
	None added	$\text{CH}_3\text{COS}(\text{CH}_2)_5\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5$ (81)			
	Peroxide	$\text{CH}_3\text{COSCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CHO}$ (90)			
	None added	$\text{CH}_3\text{COSCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{CO}_2\text{H}$ (—)			
	Peroxide	$\text{CH}_3\text{COSCH}_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ (90)			
523	None added	 (24)			
99	None added	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}(\text{SCoCH}_3)\text{C}_6\text{H}_5$ (27)			
445	None added	$\text{CH}_3\text{COS}(\text{CH}_2)_5\text{Si}(\text{C}_6\text{H}_5)_2$ (86)			
445	None added	$\text{CH}_3\text{COS}(\text{CH}_2)_5\text{Si}(\text{C}_6\text{H}_5)_2\text{CH}_3$ (96)			
528	None added	 (79)			
118	UV	CH_3 Moreadduct (17)			
		 (55)			
		$\text{CH}_3\text{CHCH}_2\text{SCoCH}_3$			
144	Parade	$\text{CH}_3\text{COSCH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COCH}_3$ (90)			

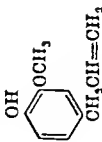
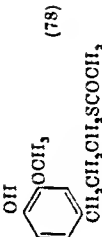
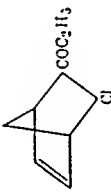
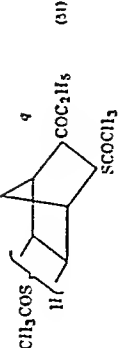
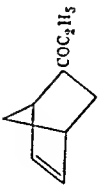
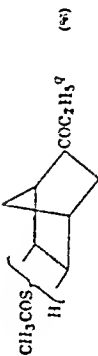
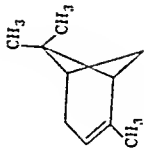
Note: References 385 to 431 are on pp. 371-376.

¹ No structure was given for this product.

² The structure was not proved.

³ The position of the acetylthio group was not determined.

TABLE X—Continued
G. Addition of Thiol Acids to Olefins—Continued

Thiol Acid Monobasic (contd.)	Olefin	Catalyst	Products (%)	Refs.
CH_3COSH (contd.)		Peroxide	 (78)	144
		None added	 q (81)	528
		None added	 q (82)	528
	 (α-α-Pinene)	None added	$\text{C}_{12}\text{H}_{18}\text{OS}^a$ (80)	519



98, 114

1,1 adduct^f (70)

UV



519

$C_{11}H_{18}OS^g$ (72)

None added



98, 114

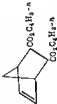





$C_{11}H_{18}OS^g$ (84)

UV

Note: References 385 to 431 are on pp. 371-376.

^f No structure was given for this product.

^g The position of the acetylthio group was not determined.

$\text{CH}_2=\text{CHC}_4\text{H}_9$ (<i>p</i> -CH ₂ =CHC ₄ H ₉) _n CH ₃	Peroxide UV	$\text{CH}_3\text{COSC}_4\text{H}_9$ (75) (<i>p</i> -CH ₂ COSC ₄ H ₉) _n CH ₃ (38)	144 148
	None added	 CO ₂ C ₄ H ₉ -n	528
$n \text{ C}_4\text{H}_9\text{CH}=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{H}$ (Oleic acid)	Peroxide	CH ₃ (CH ₂) ₁₇ CH(SCOCH ₃)(CH ₂) ₁₀ CO ₂ H (-)	531
$n \text{ C}_4\text{H}_9\text{CH}=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_3$ (Methyl oleate)	UV	CH ₃ (CH ₂) ₁₇ CH(SCOCH ₃)(CH ₂) ₁₀ CO ₂ CH ₃ (70)	532
Boulatins	None added	Vacuous syrup	112
	None added	 (100)	112
	None added	 (91)	112
$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_n\text{CH}=\text{CHCH}_3$ (Dihydromyrcene)	None added	$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_n\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCOC}_2\text{H}_5$ (79) $(\text{CH}_3)_2\text{CHCH}(\text{SCOC}_2\text{H}_5)(\text{CH}_3)_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCOC}_2\text{H}_5$ (-)	112
Squalene	None added	Vacuous syrup	112




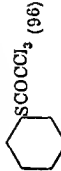






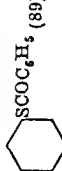


Note. References 385 to 631 are on pp 371-376

* No structure was given for this product

* The relative yields of the two products depend upon the ratio of the starting materials

TABLE X—Continued

G. Addition of Thiol Acids to Olefins—Continued

Thiol Acid	Olefin	Catalyst	Products (%)	Refs.
<i>Monobasic (cont.)</i>				
$\text{Cl}_2\text{CHCOSSH}$		None added	 (96)	112
	$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)=\text{CHCH}_3$ (Dihydromyrcene)	None added	$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)-$ $\text{CH}(\text{CH}_3)\text{SCOCHCl}_2$ $(\text{CH}_3)_2\text{CHCH}(\text{SCOCHCl}_2)(\text{CH}_2)_2\text{CH}(\text{CH}_3)-$ $\text{CH}(\text{CH}_3)\text{SCOCHCl}_2$ (2)	112
	Squalene	None added	Gum	112
		None added	 (96)	112
Cl_3CCOSSH		None added	 (100)	112
	$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{C}(\text{CH}_3)=\text{CHCH}_3$ (Dihydromyrcene)	None added	$(\text{CH}_3)_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{SCOCCl}_3$ (68) $(\text{CH}_3)_2\text{CHCH}(\text{SCOCCl}_3)(\text{CH}_2)_2\text{CH}(\text{CH}_3)-$ $\text{CH}(\text{CH}_3)\text{SCOCCl}_3$ (trace) $\text{C}_2\text{H}_5\text{COSCH}_2\text{CH}_2\text{OCH}_2\text{CH}(\text{CH}_3)_2$ (30)	112
$\text{C}_6\text{H}_5\text{COSSH}$		None added	 (61) 	99
$\text{C}_6\text{H}_5\text{COSSH}$		UV	 (89)	468
<i>Dibasic</i>				
$\text{HSCO}(\text{CH}_2)_4\text{COSSH}$	$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{CH}=\text{CH}_2$	UV	$[\text{SCO}(\text{CH}_2)_4\text{COS}(\text{CH}_2)_4]_x$ (72)	153
		None added	 (56)	499

	None added	 (64)	499
$(CH_3)_2C=CH(CH_2)_3C(CH_3)=CHOH$ (Dihydromyrcene)	None added	Viscous gum	499
Squalene	None added	Rubbery polymer	499
$CH_2=CH(CH_2)_3CH=CH_2$	UV	$[SCO(CH_2)_3COS(CH_2)_3]_n$ (61)	153
$CH_2=CH(CH_2)_3CH=CH_2$	UV	$[SCO(CH_2)_3COS(CH_2)_3]_n$ (69)	153
$CH_2=CH(CH_2)_3CH=CH_2$	UV	$[SCO(CH_2)_3COS(CH_2)_3]_n$ (75)	153
$CH_2=CH(CH_2)_3CH=CH_2$	UV	$[-SCO(CH_2)_3COS(CH_2)_3-]_n$ (92)	153
$CH_2=CH(CH_2)_3CH=CH_2$	UV	$[-SCO(CH_2)_3COS(CH_2)_3-]_n$ (22)	153
	UV	 (60)	499, 633
$CH_2=CH(CH_2)_3CH=CH_2$	UV	$[SCO(CH_2)_3COS(CH_2)_3]_n$ (65)	163
	UV	 (106)	499, 633

H. Addition of Thiol Phosphoric Acid Derivatives to Olefins

Thiol $(CH_3O)_2P(S)SH$	None added None added None added None added	$CH_2=CHCO_2CH_3$ $CH_2=CHOCOCH_3$ $CH_2=C(CH_3)CO_2CH_3$ $CHCO_2CH_3$ \parallel $CHCO_2CH_3$ $(CH_3)_2C=CHOCOCH_3$	534, 134 534, 134 534, 134 534, 134 134
	None added	$(CH_3O)_2P(S)SCH_2CH_2CO_2CH_3$ (67) $(CH_3O)_2P(S)SCH_2CH_2OCOCH_3$ (38) $(CH_3O)_2P(S)SCH_2CH(CH_3)CO_2CH_3$ (38) $(CH_3O)_2P(S)SCH(CH_3)CO_2CH_3$ (34)	
	None added	$(CH_3O)_2P(S)SCH(CH_2)_3CH_2COCH_3$ (—)	134

Note. References 385 to 631 are on pp. 371-376.

TABLE X—Continued

H. Addition of Thiol Phosphoric Acid Derivatives to Olefins—Continued

Thiol (CH ₃ O) ₂ P(S)SH (contd.)	Olefin	Catalyst	Products (%)	Refs.
	CH ₃ CCO ₂ CH ₃ CHCO ₂ CH ₃	None added	CH ₃ CHCO ₂ CH ₃ (—)	535
	CH ₂ =CHC ₆ H ₅		(CH ₃ O) ₂ P(S)SCHCO ₂ CH ₃	
	CHCO ₂ C ₂ H ₅	None added	(CH ₃ O) ₂ P(S)SCH ₂ CH ₂ C ₂ H ₅ (50)	534, 134
	CHCOO ₂ C ₂ H ₅ ClCCO ₂ C ₂ H ₅	None added	(CH ₃ O) ₂ P(S)SCHCO ₂ C ₂ H ₅ (28)	535
	CHCO ₂ C ₂ H ₅ CHCO ₂ C ₂ H ₅		ClCHCO ₂ C ₂ H ₅	
	CH ₃ CCO ₂ C ₂ H ₅ CHCO ₂ C ₂ H ₅	None added	(CH ₃ O) ₂ P(S)SCH(CO ₂ C ₂ H ₅)CH ₂ CO ₂ C ₂ H ₅ (50)	534, 134
	CH ₃ CCO ₂ C ₂ H ₅ CHCO ₂ C ₂ H ₅	None added	CH ₃ CHCO ₂ C ₂ H ₅ (25)	535
	CHCO ₂ C ₃ H ₇ -i CHCO ₂ C ₃ H ₇ -i		(CH ₃ O) ₂ P(S)SCHCO ₂ C ₂ H ₅	
	CH ₃ CCO ₂ C ₃ H ₇ -i CHCO ₂ C ₃ H ₇ -i	None added	(CH ₃ O) ₂ P(S)SCH(CO ₂ C ₃ H ₇ -i)CH ₂ CO ₂ C ₃ H ₇ -i (43)	134
	CH ₃ CCO ₂ C ₃ H ₇ -n CHCO ₂ C ₃ H ₇ -n	None added	CH ₃ CHCO ₂ C ₃ H ₇ -n (10)	535
	CH ₃ CCO ₂ C ₃ H ₇ -i CHCO ₂ C ₃ H ₇ -i	None added	(CH ₃ O) ₂ P(S)SCHCO ₂ C ₃ H ₇ -n	
	CHCO ₂ C ₃ H ₇ -i CHCO ₂ C ₃ H ₇ -i		CH ₃ CHCO ₂ C ₃ H ₇ -i (15)	535
	CHCO ₂ C ₄ H ₉ -i CHCO ₂ C ₄ H ₉ -i	None added	(CH ₃ O) ₂ P(S)SCHCO ₂ C ₃ H ₇ -i	
			(CH ₃ O) ₂ P(S)SCH(CO ₂ C ₄ H ₉ -i)CH ₂ CO ₂ C ₄ H ₉ -i (43)	134

$(C_2H_5O)_2P(S)SH$	None added	$CH_3COO_2C_2H_5$, (2)	535
$CH_2=CHCN$	None added	$(CH_3O)_2P(S)SCHCO_2C_2H_5$, $(C_2H_5O)_2P(S)SCH_2CH_2CN$ (33)	534, 134
$CH_2=CHCHO$	None added	$(C_2H_5O)_2P(S)SCH_2CH_2CHO$ (34)	134
$CH_2=CHCO_2CH_3$	None added	$(C_2H_5O)_2P(S)SCH_2CH_2CO_2CH_3$ (35)	534, 134
$CH_2=CHOCOCH_3$	None added	$(C_2H_5O)_2P(S)SCH_2CH_2OCOCH_3$ (71)	534, 134
$CH_2=C(CH_3)CO_2CH_3$	None added	$(C_2H_5O)_2P(S)SCH_2CH(CH_3)CO_2CH_3$ (69)	534, 134
$CHCO_2CH_3$	None added	$(C_2H_5O)_2P(S)SCHCO_2CH_3$ (31)	535
$ClOCO_2CH_3$		$ClCHCO_2CH_3$	
$CHCO_2CH_3$	None added	$(C_2H_5O)_2P(S)SCH(CO_2CH_3)CH_2CO_2CH_3$ (50)	134
$CHCO_2CH_3$			
$CH_2CCO_2CH_3$	None added	$CH_2CHCO_2CH_3$ (12)	535
$CHCO_2CH_3$		$(C_2H_5O)_2P(S)SCHCO_2CH_3$	
$C_2H_5CH=CH_2$	None added	$(C_2H_5O)_2P(S)SCH_2CH_2C_2H_5$ (84)	536, 534, 134
$CHCO_2CH_2CH_2Cl$	None added	$(C_2H_5O)_2P(S)SCHCO_2CH_2CH_2Cl$ (16)	535
$CHCO_2CH_2CH_2Cl$		$CH_2CO_2CH_2CH_2Cl$	
$CHCO_2C_2H_5$	None added	$(C_2H_5O)_2P(S)SCHCO_2C_2H_5$ (30)	535
$ClOCO_2C_2H_5$		$ClCHCO_2C_2H_5$	
$CHCO_2C_2H_5$	None added	$(C_2H_5O)_2P(S)SCH(CO_2C_2H_5)CH_2CO_2C_2H_5$ (55)	534, 134
$CHCO_2C_2H_5$			
$CHCO_2C_2H_5$			
$CH_2=CHC_2H_5$	Peroxide	$(C_2H_5O)_2P(S)SC_2H_5$ (75)	536

Note: References 385 to 631 are on pp 371-376.

$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_2\text{H}_5$ (14)	535
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ $(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCH}[\text{CO}_2\text{C}_2\text{H}_5]\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ (44)	134
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_2\text{H}_5$ (23)	535
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5)_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (35)	134
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_2\text{H}_5$ (22)	535
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (13)	535
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (45)	134
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (50)	534, 134
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (47)	534, 134
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (50)	534, 134
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (39)	534, 134
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (58)	537
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_2\text{H}_5\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (17)	535
$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_2\text{H}_5$	

TABLE X—Continued

II. Addition of Thiol Phosphoric Acid Derivatives to Olefins—Continued

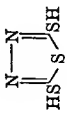



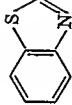
Thiol	Olefin	Catalyst	Products (%)	Refs.
$(i\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SH}$ (<i>contd.</i>)	$\text{CH}_3\text{CCO}_2\text{C}_3\text{H}_7\text{-}n$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_3\text{H}_7\text{-}n$ (16)	535
	$\text{CH}_3\text{CO}_2\text{C}_3\text{H}_7\text{-}n$	None added	$(i\text{-C}_3\text{H}_7\text{O})_2\text{P(S)SCHCO}_2\text{C}_3\text{H}_7\text{-}n$ (23)	535
	$\text{CH}_3\text{CCO}_2\text{C}_4\text{H}_9\text{-}n$	None added	$(i\text{-C}_3\text{H}_7\text{O})_2\text{P(S)SCHCO}_2\text{C}_4\text{H}_9\text{-}n$	534, 134
	$\text{CH}_3\text{CO}_2\text{C}_4\text{H}_9\text{-}n$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCH}_2\text{CH}_2\text{CN}$ (28)	134
	$\text{CH}_3\text{-CH=CHCO}$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCH}_2\text{CH}_2\text{CHO}$ (28)	134
	$\text{CH}_3\text{-CH=CHCH}_2\text{OH}$	None added	1:1 adduct ⁷ (14)	134
	$\text{CH}_3\text{-CH=CHCOCH}_3$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCH}_2\text{CH}_2\text{OCOCCH}_3$ (26)	534, 134
	$\text{CH}_3\text{-C(CH}_3\text{)CO}_2\text{CH}_3$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCH}_2\text{CH(CH}_3\text{)CO}_2\text{CH}_3$ (38)	535
	$\text{CH}_3\text{CCO}_2\text{CH}_3$	None added	$\text{CH}_3\text{CHCO}_2\text{CH}_3$ (14)	
	CHCO_2CH_3	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCHCO}_2\text{CH}_3$	537, 534, 134
	$\text{C}_6\text{H}_5\text{CH=CH}_2$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCH}_2\text{CH}_2\text{C}_6\text{H}_5$ (31)	534, 134
	$\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$ (40)	
	$\text{CHCO}_2\text{C}_3\text{H}_7$	None added	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	537
	$\text{CH}_3\text{-CH=CHC}_6\text{H}_{13}\text{-}n$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SC}_6\text{H}_{13}\text{-}n$ (31)	535
	$\text{CH}_3\text{CCO}_2\text{C}_2\text{H}_5$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_2\text{H}_5$ (11)	
	$\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCHCO}_2\text{C}_2\text{H}_5$	535
	$\text{CH}_3\text{CCO}_2\text{C}_3\text{H}_7\text{-}n$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_3\text{H}_7\text{-}n$ (11)	
	$\text{CHCO}_2\text{C}_3\text{H}_7\text{-}n$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCHCO}_2\text{C}_3\text{H}_7\text{-}n$ (11)	535
	$\text{CH}_3\text{CCO}_2\text{C}_4\text{H}_9\text{-}n$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_4\text{H}_9\text{-}n$	
	$\text{CHCO}_2\text{C}_4\text{H}_9\text{-}n$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCHCO}_2\text{C}_4\text{H}_9\text{-}n$	535
	$\text{CH}_3\text{CCO}_2\text{C}_5\text{H}_{11}\text{-}i$	None added	$\text{CH}_3\text{CHCO}_2\text{C}_5\text{H}_{11}\text{-}i$ (25)	535
	$\text{CHCO}_2\text{C}_5\text{H}_{11}\text{-}i$	None added	$(n\text{-C}_4\text{H}_9\text{O})_2\text{P(S)SCHCO}_2\text{C}_5\text{H}_{11}\text{-}i$	

$(t-C_4H_9O)_4P(S)SH$	$CH_2=CHCN$ $CH_2=CHCO_2CH_3$ $CH_2=CHCOCH_3$ $CH_2=C(CH_3)CO_2CH_3$	None added None added None added None added	$(t-C_4H_9O)_4P(S)SCH_2CH_2CN$ (44) $(t-C_4H_9O)_4P(S)SCH_2CH_2CO_2CH_3$ (56) $(t-C_4H_9O)_4P(S)SCH_2CH_2COCH_3$ (43) $(t-C_4H_9O)_4P(S)SCH_2CH(CH_3)CO_2CH_3$ (56)	534, 134 534, 134 534, 134 534, 134
	$CH_3CO_2C_2H_5$ \parallel $CHCO_2C_2H_5$	None added	$CH_3CHCO_2C_2H_5$ (13)	535
	$C_4H_9CH=CH_2$	None added	$(t-C_4H_9O)_4P(S)SCHCO_2C_2H_5$	534, 134
	$CHCO_2C_2H_5$ \parallel $CHCO_2C_2H_5$	None added	$(t-C_4H_9O)_4P(S)SCHCO_2C_2H_5$ (15)	534, 134
	$CH_3OCO_2C_2H_5$ \parallel $CHCO_2C_2H_5$	None added	$CH_3CO_2C_2H_5$ \parallel $CH_3CHCO_2C_2H_5$ (22)	535
	$CH_3=CHCN$ $CH_2=CHCO_2CH_3$ $CH_2=C(CH_3)CO_2CH_3$	None added None added None added	$(p-C_6H_4O)_4P(S)SCHCO_2C_2H_5$ $(p-ClC_6H_4O)_4P(S)SCH_2CH_2CN$ (53) $(p-ClC_6H_4O)_4P(S)SCH_2CH_2CO_2CH_3$ (46) $(p-ClC_6H_4O)_4P(S)SCH_2CH(CH_3)CO_2CH_3$ (74)	535 535 535 535
	$CHCO_2C_2H_5$ \parallel $CHCO_2C_2H_5$	None added	$(p-ClC_6H_4O)_4P(S)SCHCO_2C_2H_5$ (44) \parallel $CH_3CO_2C_2H_5$	535
	$CH_2=CHCO_2CH_3$ $CH_2=C(CH_3)CO_2CH_3$	None added None added	$(C_4H_9O)_4P(S)SCH_2CH_2CN$ (45) $(C_4H_9O)_4P(S)SCH_2CH_2CO_2CH_3$ (47) $(C_4H_9O)_4P(S)SCH_2CH(CH_3)CO_2CH_3$ (73)	535 535 535
	$CHCO_2C_2H_5$ \parallel $CHCO_2C_2H_5$	None added	$(C_4H_9O)_4P(S)SCHCO_2C_2H_5$ (54) \parallel $CH_3CO_2C_2H_5$	535
	$CH_2=CHC_2H_5$ $CH_2=CHC_2H_5$ $CH_2=CHC_2H_5$	None added None added None added	$(n-C_4H_9O)_4P(S)SCH_2CH_2C_2H_5$ (79) $(n-C_4H_9O)_4P(S)SC_2H_5$ (87)	537 537

Note - References 385 to 431 are on pp. 371-376.

f No structure was given for this product.


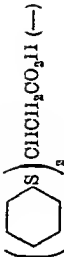
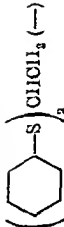
TABLE X—Continued
I. Addition of Heterocyclic Thiols to Olefins





Thiol	Olefin	Catalyst	Products (%)	Refs.
	$C_6H_5CH=CH_2$	None added	$C_6H_5CH_2CH_2S\text{---}\text{N}=\text{N}\text{---}SH$ (92)	538
		None added	$SCH(CO_2H)CH_2CO_2H$ (96)	539
	$C_6H_5CH=CH_2$	None added	$SCH_2CH_2C_6H_5$ (67)	539
	$CH_2=CHSO_2C_6H_4CH_3 \cdot p$	None added	 $SCH_2CH_2SO_2C_6H_4CH_3 \cdot p$	447, 506

J. Addition of Aliphatic Thiols to Acetylenes

Thiol	Acetylene	Catalyst	Products (%)	Refs.
CH_3SH	$HC\equiv CH + CO$ (890-900 atm.)	Azonitrile	$CH_3SCH=CHCHO$ (4)	540
	$HC\equiv CCH_2OH$	Azonitrile + UV	$CH_3SCH_2CH_2SCH_3$ (—)	184
	$HC\equiv CC_6H_5$	None added	$C_6H_5CH=CHSC_6H_5$ (42)	541, 542
	$HC\equiv CH$	Peroxide	$C_2H_5SCH_2CH_2SC_2H_5$ (50)	175
	$HC\equiv CCO_2H$	Peroxide + UV	$C_2H_5SCH=CHCO_2H$ (—)	170
	$HC\equiv CCH_2OH$	Peroxide + UV	$C_2H_5SCH_2CH(CO_2H)SC_2H_5$ (—)	170
	$HC\equiv COC_2H_5$	None added	$C_2H_5SCH_2CH(CH_2OH)SC_2H_5$ (95) $C_2H_5OCH=CHSC_2H_5$ (22-84) (<i>cis</i> and <i>trans</i>)	106, 543
	$HC\equiv CSC_2H_5$	None added	$C_6H_5OCH(SC_2H_5)CH_2SC_2H_5$ (6-64)	544
	$CH_3CO_2CH_2C\equiv CH$	Peroxide + UV	$C_2H_5SCH=CHSC_2H_5$ (59)	170
	$CH_3C\equiv CCO_2H_5$	Peroxide + UV	$CH_3CO_2CH_2CH(SC_2H_5)CH_2SC_2H_5$ (93)	545
	$(CH_3)_2C(OH)C\equiv CH$	azonitrile	$C_2H_5SC(CH_3)=CHOC_2H_5$ (74)	170
		Peroxide + UV	$(CH_3)_2C(OH)CH(SC_2H_5)CH_2SC_2H_5$ (72)	170

TABLE X—Continued
J. Addition of Aliphatic Thiols to Acetylenes—Continued

Thiol	Acetylene	Catalyst	Products (%)	Refs.
$n\text{-C}_2\text{H}_5\text{SH}$ (contd.)		Peroxide	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SC}_2\text{H}_5)_2 = \text{CHOC}_2\text{H}_5$ (50)	172
$(\text{CH}_3)_2\text{CHSH}$	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{COC}_2\text{H}_5$	Peroxide	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SC}_2\text{H}_5)_2 = \text{CHOC}_2\text{H}_5$ (80)	172
$n\text{-C}_4\text{H}_9\text{SH}$	$\text{HC}\equiv\text{CH}$	Peroxide	$n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (83)	175
	$\text{HC}\equiv\text{CH} + \text{CO}$	Peroxide	$n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (17)	175
	(2450–2950 atm.)		$n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (32)	184
	$\text{HC}\equiv\text{CCl}_2\text{OH}$	Mercuric acetate + UV	$n\text{-C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (50)	551
	$\text{HC}\equiv\text{CCl}=\text{CHSCl}_2$	Azonitrile	$\text{CH}_3\text{SCH}_2=\text{CHCH}=\text{CHSCl}_2$ (22)	
			$\text{CH}_3\text{SCH}_2=\text{CHCH}=\text{CHSC}_2\text{H}_5$ (33)	
			$n\text{-C}_4\text{H}_9\text{SCH}_2=\text{CHCH}=\text{CHSC}_2\text{H}_5$ (12)	
	$\text{HC}\equiv\text{CCl}=\text{CHSC}_2\text{H}_5$	Azonitrile	$\text{C}_6\text{H}_5\text{SCH}_2=\text{CHCH}=\text{CHSC}_2\text{H}_5$ (34)	551
			$\text{C}_6\text{H}_5\text{SCH}_2=\text{CHCH}=\text{CHSC}_2\text{H}_5$ (44)	
			$n\text{-C}_4\text{H}_9\text{SCH}_2=\text{CHCH}=\text{CHSC}_2\text{H}_5$ (20)	
	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{COC}_2\text{H}_5$	Peroxide	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SC}_2\text{H}_5)_2 = \text{CHOC}_2\text{H}_5$ (31)	172
	$\text{C}_6\text{H}_5\text{C}\equiv\text{CH} + \text{CO}$	Azonitrile	$n\text{-C}_4\text{H}_9\text{SCH}_2=\text{CHCH}=\text{CHOC}_2\text{H}_5$ (9)	540
	(800–900 atm.)			
	$\text{HC}\equiv\text{CCl}=\text{CHSO}_2\text{H}_9$	Azonitrile	$n\text{-C}_4\text{H}_9\text{SCH}_2=\text{CHCH}=\text{CHSC}_2\text{H}_5$ (75)	551
	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{COC}_2\text{H}_5$	Peroxide	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SC}_2\text{H}_5)_2 = \text{CHOC}_2\text{H}_5$ (80)	172
	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{COC}_2\text{H}_5$	Peroxide	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SC}_2\text{H}_5)_2 = \text{CHOC}_2\text{H}_5$ (82)	172
	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{COC}_2\text{H}_5$	Peroxide	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SC}_2\text{H}_5)_2 = \text{CHOC}_2\text{H}_5$ (93)	172
	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}\equiv\text{COC}_2\text{H}_5$	Peroxide	$(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SC}_2\text{H}_5)_2 = \text{CHOC}_2\text{H}_5$ (92)	172
	$\text{HC}\equiv\text{CCO}_2\text{H}$	None added	 (39)	101
			(<i>cis</i> und <i>trans</i>)	
			 (—)	
			 (—)	






$\text{C}_6\text{H}_5\text{CH}_2\text{SH}$	$\text{HO}_2\text{CO}_2\text{C}\equiv\text{CCO}_2\text{H}, \text{H}_2\text{O}$	None added	 (trans) 	104
$\text{C}_6\text{H}_5\text{CH}_2\text{SR}$	$(\text{CH}_3)_3\text{C}(\text{OH})\text{C}\equiv\text{COC}_6\text{H}_5$	Peroxide	$(\text{CH}_3)_3\text{C}(\text{OH})\text{C}\equiv\text{CHOC}_6\text{H}_5$ (89) 	172
$p\text{-C}_6\text{H}_4\text{SH}$	$\text{HO}\equiv\text{CH}$ $\text{HO}\equiv\text{CH} + \text{CO}$ (960-1000 atm) $\text{HO}\equiv\text{CCO}_2\text{H}$ $\text{HO}\equiv\text{CCH}_2\text{OH}$	Azonitrile Azonitrile	$\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (94) $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (95) $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (78) $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (30)	175 175 175 175
$n\text{-C}_6\text{H}_{13}\text{SH}$	$\text{C}_6\text{H}_5\text{OC}\equiv\text{CH}$ $\text{HO}\equiv\text{CSC}_6\text{H}_5$	Peroxide Mercuric acetate + UV	$\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{CH}(\text{CH}_3\text{OH})\text{SCH}_2\text{C}_6\text{H}_5$ (30)	105 184
$n\text{-C}_6\text{H}_{13}\text{SH}$	$(\text{CH}_3)_3\text{C}(\text{OH})\text{C}\equiv\text{COC}_6\text{H}_5$	None added	$\text{C}_6\text{H}_5\text{OCH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (74)	106
$n\text{-C}_6\text{H}_{13}\text{SH}$	$(\text{CH}_3)_3\text{C}(\text{OH})\text{C}\equiv\text{CSC}_6\text{H}_5$	None added	$\text{C}_6\text{H}_5\text{OCH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (49)	544
$(\text{C}_6\text{H}_5)_3\text{CSH}$	$\text{C}_6\text{H}_5\text{OC}\equiv\text{CH}$	None added	$(\text{CH}_3)_3\text{COH}(\text{CSC}_6\text{H}_5)_2\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (76)	172, 643
$(\text{C}_6\text{H}_5)_3\text{CSH}$	$(\text{CH}_3)_3\text{C}(\text{OH})\text{C}\equiv\text{COC}_6\text{H}_5$	Peroxide	$\text{C}_6\text{H}_5\text{OCH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (33)	544
$(\text{C}_6\text{H}_5)_3\text{CSH}$	$(\text{CH}_3)_3\text{C}(\text{OH})\text{C}\equiv\text{CSC}_6\text{H}_5$	None added	$\text{C}_6\text{H}_5\text{OCH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (84)	106
$(\text{C}_6\text{H}_5)_3\text{CSH}$	$\text{HO}\equiv\text{CSC}_6\text{H}_5$	Peroxide	$(\text{CH}_3)_3\text{COH}(\text{CSC}_6\text{H}_5)_2\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (77)	172
$(\text{C}_6\text{H}_5)_3\text{CSH}$	$\text{HO}\equiv\text{CSC}_6\text{H}_5$	None added	$(\text{CH}_3)_3\text{COH}(\text{CSC}_6\text{H}_5)_2\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ (87)	172
$\text{HSCH}_2\text{CH}_2\text{SH}$	$\text{CH}_3\text{CO}_2\text{CH}_2\text{C}\equiv\text{CC}_6\text{H}_5\text{COOCH}_3$	Peroxide + UV	 + polystyrene	544 170

Notes: References 385 to 631 are on pp 371-376.

TABLE X—Continued

K. Addition of Thiol Acids to Acetylenes

Thiol	Acetylene	Catalyst	Products (%)	Refs.
CH_3COSH	$\text{HC}\equiv\text{CCO}_2\text{H}$	None added	$\text{CH}_3\text{COSCH}=\text{CHCO}_2\text{H}$ (—) (<i>cis</i> and <i>trans</i>)	105
	$\text{HC}\equiv\text{CCH}_2\text{OH}$	Azonitrile + UV	+ diadduct $\text{CH}_3\text{COSCH}=\text{CHCH}_2\text{OH}$ (10) $\text{CH}_3\text{COSCH}_2\text{CH}(\text{CH}_2\text{OH})\text{SCOCH}_3$ (63)	174, 170
	$\text{HO}_2\text{C}\equiv\text{CCO}_2\text{H}$ $\text{HC}\equiv\text{CCO}_2\text{CH}_3$	None added None added	$\text{HO}_2\text{CCH}(\text{SCOCH}_3)\text{CH}(\text{CO}_2\text{H})\text{SCOCH}_3$ (67) $\text{CH}_3\text{COSCH}=\text{CHCO}_2\text{CH}_3$ <i>cis</i> (8)	105 105
	$\text{HC}\equiv\text{C}(\text{CH}_2)_2\text{Cl}$	Peroxide	<i>trans</i> (18) $\text{CH}_3\text{COSCH}_2\text{CH}(\text{CO}_2\text{CH}_3)\text{SCOCH}_3$ (17) $\text{CH}_3\text{COSCH}_2\text{CH}(\text{SCOCH}_3)\text{CH}_2\text{CH}_2\text{Cl}$ (—)	552
	$\text{HC}\equiv\text{CCH}_2\text{OCH}_3$	Peroxide	$\text{CH}_3\text{COSCH}=\text{CH}(\text{CH}_2)_2\text{Cl}$ (—) $\text{CH}_3\text{COSCH}=\text{CHCH}_2\text{OCH}_3$ (15)	171
	$\text{HC}\equiv\text{CSC}_2\text{H}_5$ $\text{HC}\equiv\text{COH}_2\text{OCOCH}_3$	None added Azonitrile	$\text{CH}_3\text{COSCH}_2\text{CH}(\text{SCOCH}_3)\text{CH}_2\text{OCH}_3$ (36) $\text{CH}_3\text{COSCH}=\text{CHSC}_2\text{H}_5$ (42) $\text{CH}_3\text{COSCH}_2\text{CH}(\text{SCOCH}_3)\text{CH}_2\text{OCOCH}_3$ (10) $\text{CH}_3\text{COSCH}_2\text{CH}(\text{SCOCH}_3)\text{CH}_2\text{OCOCH}_3$ (65)	544 174
	$\text{HC}\equiv\text{CCl}_2\text{CHOHCH}_3$ $\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$ $\text{HC}\equiv\text{CClHOHCH}=\text{CHCH}_3$	Peroxide None added Peroxide	$\text{CH}_3\text{COSCH}=\text{CHCH}_2\text{CHOHCH}_3$ (60) $\text{CH}_3\text{O}_2\text{CCH}(\text{SCOCH}_3)\text{CH}(\text{CO}_2\text{CH}_3)\text{SCOCH}_3$ (58) $\text{HC}\equiv\text{CClHOHCH}_2\text{CH}(\text{OH})\text{SCOCH}_3$ (26)	173 105 173
	$\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{OCOCH}_3$ $\text{HC}\equiv\text{CC}_2\text{H}_5$	Peroxide Peroxide	$\text{CH}_3\text{COSCH}_2\text{CH}(\text{SCOCH}_3)\text{CH}(\text{OH})\text{CH}=\text{CHCH}_3$ (11) $\text{CH}_3\text{COSCH}=\text{CHCH}_2\text{CH}_2\text{OCOCH}_3$ (27) $\text{CH}_3\text{COSCH}=\text{CHC}_2\text{H}_5$, <i>n</i> (up to 64) $\text{CH}_3\text{COSCH}_2\text{CH}(\text{SCOCH}_3)\text{C}_2\text{H}_5$, <i>n</i> (up to 70)	552 171, 519
	$\text{HC}\equiv\text{CC}(\text{CH}_3)_3$ $\text{HC}\equiv\text{CClHOHC}_2\text{H}_4$	None added None added	$\text{CH}_3\text{COSCH}=\text{CHC}(\text{CH}_3)_3$ (—) $\text{CH}_3\text{COSCH}=\text{CHCHONC}_2\text{H}_4$, <i>n</i> (up to 67)	519 173
	$\text{HC}\equiv\text{CC}_2\text{H}_5$	None added	$\text{CH}_3\text{COSCH}_2\text{CH}(\text{SCOCH}_3)\text{CHOHC}_2\text{H}_4$, <i>n</i> (15) $\text{CH}_3\text{COSCH}=\text{CHC}_2\text{H}_5$ (86)	519, 171, 542



$\text{HO}=\text{C}(\text{CH}_3)_2\text{O}=\text{CH}$	None added	$\text{HO}=\text{C}(\text{CH}_3)_2\text{CH}=\text{CHSCOOCH}_3$ (26) $\text{HO}=\text{C}(\text{CH}_3)_2\text{CH}(\text{SCOOCH}_3)\text{CH}_2\text{SCOOCH}_3$ (12) $\text{CH}_3\text{COSCH}=\text{CH}(\text{CH}_3)_2\text{CH}(\text{SCOOCH}_3)\text{CH}_2\text{SCOOCH}_3$ (30)	171
	None added	 $\text{CH}(\text{SCOOCH}_3)\text{CH}_2\text{SCOOCH}_3$ (up to 4t)	519
	Peroxide	 + dehydration product (57)	173
	None added None added UV	 $\text{CH}(\text{SCOOCH}_3)\text{CH}_2\text{SCOOCH}_3$ (4)	519 519 173
$\text{HO}=\text{C}(\text{CH}_3)_2\text{O}=\text{CH}$	None added None added UV	$\text{CH}_3\text{COSCH}=\text{CHC}_6\text{H}_5$ (65) $\text{C}_6\text{H}_5\text{CH}(\text{SCOOCH}_3)\text{CH}(\text{CO}_2\text{H})\text{SCOOCH}_3$ (—) $\text{C}_6\text{H}_5\text{CH}(\text{CH}=\text{CHSCOOCH}_3)\text{CH}_2\text{SCOOCH}_3$ (24) $\text{C}_6\text{H}_5\text{CH}(\text{CH}=\text{CHSCOOCH}_3)\text{CH}_2\text{SCOOCH}_3$ (11) $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CHSCOOCH}_3$ (74) $i\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{CHSCOOCH}_3$ (74) $\text{HO}=\text{C}(\text{CH}_3)_2\text{CH}=\text{CHSCOOCH}_3$ (65) $\text{C}_6\text{H}_5\text{COSCH}=\text{CHC}_6\text{H}_5$ (—) $\text{C}_6\text{H}_5\text{COSCH}=\text{CHCHO}$ (18-20) $\text{C}_6\text{H}_5\text{COSCH}=\text{CHSC}_2\text{H}_5$ (14) $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{SCOC}_2\text{H}_5)_2=\text{CHSC}_2\text{H}_5$ (24) $\text{C}_6\text{H}_5\text{COSCH}=\text{CHC}_6\text{H}_5$ (—)	171 174 553 519 519 544 544 519

Note: References 385 to 531 are on pp. 371-376.

* The structure was not proved.


TABLE X—Continued

L. Addition of Aromatic Thiols to Acetylenes

Thiol	Acetylene	Catalyst	Products (%)	Refs.
C_6H_5SH	$HC \equiv CH + CO$ (920–960 atm.) $HC \equiv CCH_2OH$	Azonitrile	$C_6H_5SCH=CHCHO$ (9)	175
		Mercuric acetate + UV	$C_6H_5SCH_2CH_2SC_6H_5$ (63) $C_6H_5SCH_2CH(CH_2OH)SC_6H_5$ (40)	184
	$(CH_3)_2C(OH)C \equiv COC_6H_5$ $HC \equiv CC_6H_5$ $HC \equiv CCH=CHSC_6H_5$	Peroxide None added Azonitrile	$(CH_3)_2C(OH)C(SC_6H_5)=CHOC_2H_5$ (86) $C_6H_5SCH=CHC_6H_5$ (97) $C_6H_5SCH=CHCH=CHSC_6H_5$ (94)	172 541 550
	$HC \equiv CCH=CHO$ 	Azonitrile	$C_6H_5SCH=CHCH=CHO$  (93)	549
$p\text{-}BrC_6H_4SH$ $p\text{-}ClC_6H_4SH$ $p\text{-}CH_3C_6H_4SH$ $p\text{-}CH_3CONHC_6H_4SH$ $p\text{-}i\text{-}C_4H_9C_6H_4SH$	$HC \equiv CCH=CHOC_6H_5$ $(CH_3)_2C(OH)C \equiv COC_2H_5$ $HC \equiv CSC_2H_5$ $(CH_3)_2C(OH)C \equiv COC_2H_5$ $(CH_3)_2C(OH)C \equiv COC_2H_5$ $HC \equiv CC_2H_5$ $C_6H_5OC \equiv COC_2H_5$ $(CH_3)_2C(OH)C \equiv COC_2H_5$	Azonitrile Peroxide None added Peroxide Peroxide None added None added Peroxide	$C_6H_5SCH=CHCH=CHOC_6H_5$ (81) $(CH_3)_2C(OH)C(SC_6H_4Br-p)=CHOC_2H_5$ (87) $p\text{-}ClC_6H_4SCH=CHSC_2H_5$ (59) $(CH_3)_2C(OH)C(SC_6H_4Cl-p)=CHOC_2H_5$ (75) $(CH_3)_2C(OH)C(SC_6H_4CH_3-p)=CHOC_2H_5$ (72) $p\text{-}CH_3C_6H_4SCH=CHC_6H_5$ (100) $p\text{-}CH_3CONHC_6H_4SCH=CHOC_2H_5$ (—) $(CH_3)_2C(OH)C(SC_6H_4C_4H_9-i-p)=CHOC_2H_5$ (96)	549 172 544 172 172 554, 541 555 172

M. Addition of Hydrogen Sulfide to Olefins and Acetylenes

Olefin	Moles H_2S : Mole Olefin	Catalyst	Products (%)	Refs.
$CF_2=CFCl$	1.02	UV	$CHFClCF_2SH$ (43) $(CHFClCF_2)_2S$ (10) $(CHFClCF_2)_2S_2$ (31)	198, 199a
$CH_2=CHCl$	~ 1	UV	CH_2ClCH_2SH { (70–80) $(CH_2ClCH_2)_2S$ }	556, 191
$CH_2=CHSiCl_3$ $CF_3=CF_2$	0.5 1	None added UV	$(CH_3SiCH_2CH_2)_2S$ (50) CHF_2CF_2SH (—) $(CHF_2CF_2)_2S$ (—) $(CHF_2CF_2)_2S_2$ (—)	209 198, 199a

$\text{CH}_2=\text{CH}_2$		None added	$\text{C}_6\text{H}_5\text{SH}$ (14) $(\text{C}_6\text{H}_5)_2\text{S}$ (47) $n\text{-C}_4\text{H}_9\text{SC}_2\text{H}_5$ (1) $(\text{C}_2\text{H}_5)_2\text{S}$ (16) $\text{C}_4\text{H}_9\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SC}_2\text{H}_5$ (18) $(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{S}$ $n\text{-C}_4\text{H}_9\text{SH}$ (62) $(n\text{-C}_4\text{H}_9)_2\text{S}$ (23)	189 81 657 191, 558, 559, 560, 453, 201 190
$\text{CH}_2=\text{CH}_2 + \text{CO}$ (3000 atm.)	1 2	None added UV		
$\text{CH}_2=\text{CHNH}_2$				
$\text{CH}_2=\text{CH}_2$				
$\text{HOCH}_2\text{CH}=\text{CH}_2$	2 5	Acetonitrile	$\text{HO}(\text{CH}_2)_2\text{SH}$ (39) $[\text{HO}(\text{CH}_2)_3\text{S}]_n$ (39) $\text{NH}_2(\text{CH}_2)_2\text{SH}$ (22) $[\text{NH}_2(\text{CH}_2)_3\text{S}]_n$ (31) Polymer* (93) (mol wt = 1000-1100)	190 202 195
$(\text{CH}_2=\text{CH})_2\text{O}$	3 5	Acetonitrile	$\text{HSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH}$ (47) $\text{HSCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{SH}$ (27) $\text{HSC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SH}$ (17) $\text{CH}_3\text{CH}(\text{SH})\text{CHCH}_3$ $n\text{-C}_4\text{H}_9\text{SH}$ (63) $(n\text{-C}_4\text{H}_9)_2\text{S}$ (12) $\text{CH}_3\text{CH}(\text{SH})\text{C}_2\text{H}_5$ (17) $(\text{C}_2\text{H}_5)_2\text{CHCH}_2\text{SH}$ (3) $(\text{CH}_3)_2\text{CHCH}_2\text{SH}$ (62) $[(\text{CH}_3)_2\text{CHCH}_2]_n\text{S}$ (8) $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{SH}$ (59) $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ (26) $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OC}_2\text{H}_5$ (2) $\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2\text{SH}$ (59) $(\text{C}_2\text{H}_5\text{SCH}_2\text{CH}_2)_n\text{S}$ (40)	191, 555 191, 558 201 201 197 179
$\text{CH}_2\text{CH}=\text{CHCH}_3$ $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	2	UV UV		
$\text{CH}_3\text{CH}=\text{CHCH}_3$	4 4	Peroxide (H_2O)		
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	4 5	Peroxide (H_2O)		
$\text{C}_6\text{H}_5\text{OCH}=\text{CH}_2$	1 4	O_3		
$\text{C}_6\text{H}_5\text{SCH}=\text{CH}_2$	1 5	O_3		
		UV	 trans (12) cis (61)	561

Note: References 385 to 631 are on pp 371-376.

* No structure was given for this product.

TABLE X—Continued
M. Addition of Hydrogen Sulfide to Olefins and Acetylenes—Continued


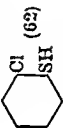
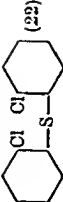
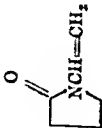
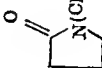
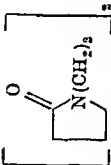

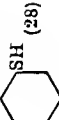
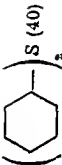

Olefin	Moles H ₂ S: Moles Olefin	Catalyst	Products (%)	Refs.
$n\text{-C}_3\text{H}_7\text{OCH=CH}_2$	1.2	None added	$n\text{-C}_3\text{H}_7\text{OCH}_2\text{CH}_2\text{SH}$ (61) $n\text{-C}_3\text{H}_7\text{O}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{OC}_3\text{H}_7$ -n (2S) $n\text{-C}_3\text{H}_7\text{OCH}(\text{CH}_3)\text{S}(\text{CH}_2)_2\text{OC}_3\text{H}_7$ -n (6) (CH ₃) ₂ CHOCH ₂ CH ₂ SH (59) (CH ₃) ₂ CHOCH(CH ₃)S(CH ₂) ₂ OCH(CH ₃) ₂ (25) (CH ₃) ₂ CHOCH(CH ₃)S(CH ₂) ₂ OCH(CH ₃) ₂ (10) (CH ₃) ₂ Si(CH ₂) ₂ SH (68) [(CH ₃) ₂ Si(CH ₂) ₂] ₂ S (8)	197
(CH ₃) ₂ CHOCN=CH ₂	1	None added		197
(CH ₃) ₂ SiCH=CH ₂		UV		209
	90	UV	 (62) (<i>cis</i> and <i>trans</i>)  (22)	97
		Azonitrile	 N(CH ₂) ₂ SH (0-10)	562
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH=CH}_2$		UV	 S (64-87) Liquid polymer (Av. mol. wt. = 210)	191
		Azonitrile or peroxido	 (28)  S (40)	190, 201

TABLE X—Continued
M. Addition of Hydrogen Sulfide to Olefins and Acetylenes—Continued

Olefin	Moles H ₂ S: Mole Olefin	Catalyst	Products (%)	Refs.
		Azonitrilo		562
$(\text{CH}_3)_2\text{C}=\text{CHCH}=\text{C}(\text{CH}_3)_2$	4.9	Peroxido + Iron	$(\text{CH}_3)_2\text{C}=\text{CHCH}(\text{SH})\text{CH}(\text{CH}_3)_2$ (18) $(\text{CH}_3)_2\text{CHCH}(\text{SH})\text{CH}(\text{SH})\text{CH}(\text{CH}_3)_2$ (15)	103
	1.2	Azonitrilo		200, 197
$[\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2]_2\text{O}$	1	UV	Polymer (83)	202, 205
$[\text{CH}_2=\text{CHOC}(\text{CH}_3)_2]_2\text{O}$	2.8	γ -Rays	(Av. mol. wt. = 661) $(\text{HSCH}_2\text{CH}_2\text{OC}(\text{CH}_3)_2)_2\text{O}$ (70)	204
$n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	2.9	γ -Rays	$n\text{-C}_6\text{H}_{17}\text{SH}$ (88)	204
		Azonitrilo	$n\text{-C}_6\text{H}_{17}\text{SH}$ (73)	190
$n\text{-C}_8\text{H}_{17}\text{CH}=\text{CHCH}_3$		Azonitrilo	$n\text{-C}_8\text{H}_{17}\text{S}$ (24) $\text{C}_8\text{H}_{17}\text{SH}$ (66)	190
$(\text{C}_2\text{H}_5\text{O})_2\text{SiCH}=\text{CH}_2$		UV	$(\text{C}_2\text{H}_5)_2\text{SiS}'$ (15)	209
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2$	0.7	Peroxido (H ₂ O)	$(\text{C}_2\text{H}_5\text{O})_2\text{SiCH}_2\text{CH}_2\text{SH}$ (5) $[(\text{C}_2\text{H}_5\text{O})_2\text{SiCH}_2\text{CH}_2\text{S}]_2$ (50) $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{SH}$ (29) $[\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{S}]_2$ (2)	201
	6	Azonitrilo		190

(CH ₃) ₂ C=CH(CH ₃) ₂ C(CH ₃)=CHCH ₃	1:1	Acetone + UV	(CH ₃) ₂ CHCH(SH)(CH ₃)C(CH ₃)=CHCH ₃ (CH ₃) ₂ C=CH(CH ₃)CH(CH ₃)SH	194
				(22)
n C ₁₀ H ₁₇ OCH=CH ₂	1:55	None added	C ₁₀ H ₁₇ S ₂ (2) C(CH ₃) ₂ CHCH(SH)(CH ₃)CH(CH ₃)CH(CH ₃)SH (2) n C ₁₀ H ₁₇ OCH ₂ CH ₂ SH (69) (n C ₁₀ H ₁₇ OCH ₂ CH ₂) ₂ S (21)	197
p (CH ₃) ₂ CC ₂ H ₄ OCH=CH ₂	2:1	Azonitrile	p (CH ₃) ₂ CC ₂ H ₄ OCH ₂ CH ₂ SH (36) p (CH ₃) ₂ CC ₂ H ₄ OCH ₂ CH ₂ (CH ₂) ₂ S (54)	200
n C ₁₀ H ₁₇ OK=CH ₂		Peroxide (H ₂ O)	n C ₁₀ H ₁₇ SH (57) (n C ₁₀ H ₁₇) ₂ S (19)	201
CH ₂ =C(CO ₂ C ₂ H ₅ n)(CH ₃) ₂ CH(CH ₃)CO ₂ C ₂ H ₅ n		Peroxide	CH(CH ₃)CO ₂ C ₂ H ₅ n(CH ₃) ₂ HSCH ₂ CH(CO ₂ C ₂ H ₅ n)(CH ₃) ₂ (n C ₁₀ H ₁₇ OCH ₂ CH ₂) ₂ S (19) C(CH ₃) ₂ CHCH(SH)(CH ₃)CO ₂ C ₂ H ₅ n (—) C(CH ₃) ₂ CHCH(SH)(CH ₃)CO ₂ C ₂ H ₅ n (—) C(CH ₃) ₂ CHCH(SH)(CH ₃)CO ₂ C ₂ H ₅ n (—) (n C ₁₀ H ₁₇) ₂ S (19) C(CH ₃) ₂ CHCH(SH)(CH ₃)CO ₂ C ₂ H ₅ n (77)	206
n C ₁₄ H ₂₉ CH=CH ₂	7:3	Azonitrile	n C ₁₄ H ₂₉ SH (72) (n C ₁₄ H ₂₉) ₂ S (15)	190, 177 365, 438 190
CH ₂ =CH(CH ₃)CO ₂ H n C ₁₄ H ₂₉ CH=CH ₂	9:5	Azonitrile	n C ₁₄ H ₂₉ SH (69) (n C ₁₄ H ₂₉) ₂ S (23)	190
CH ₂ (CH ₃)CH=CH(CH ₃) ₂ CO ₂ CH(CH ₃) ₂		Azonitrile	CH ₂ (CH ₃)CH(SH)(CH ₃)CO ₂ CH(CH ₃) ₂ (73)	190
Acetylene CF ₃ C≡CH	Moles H ₂ S: Mole Acetylene 2:5	Catalyst X ray	Products (%) CF ₃ CH=CHSH (73) (cis and trans) CF ₃ CHSHCH ₂ SH (20) (CF ₃ CH=CH) ₂ S (5)	Rafn. 208a




Note. References 365 to 431 are on pp. 371-376.
/ No structure was given for this product.

TABLE X—Continued
M. Addition of Hydrogen Sulfide to Olefins and Acetylenes—Continued

Acetylene	Moles H ₂ S: Mole Acetylene	Catalyst	Products (%)	Refs.
CH ₃ C≡CH	2	X-ray	CH ₃ CH=CHSH (32) (<i>cis</i> and <i>trans</i>) CH ₃ CHSHCH ₂ SH (36) Polymer (33)	208a
CF ₃ C≡CCF ₃ CH ₃ C≡CClH ₂	3.3 1.8	X-ray X-ray	CF ₃ CH=C(SH)CF ₃ (60) CH ₃ CH=C(SH)CH ₂ (24) (<i>cis</i> and <i>trans</i>) CH ₃ CHSHCHSHCH ₂ (41) Polymer (36)	208a 208a
C ₆ H ₅ C≡CH	3.3	X-ray	C ₆ H ₅ CH=CHSH (8) (C ₆ H ₅ CH=CH) ₂ S (47) Polymer (46)	208a


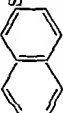
N. Addition of Disulfide to Olefins and Acetylenes

Olefin	Disulfide	Catalyst	Products (%)	Refs.
CF ₃ =CF ₂	NaHSO ₃	None or peroxide	CH ₂ CF ₂ SO ₂ Na (—)	566
CF ₃ =CH ₂	NaHSO ₃	None added	CH ₂ CF ₂ SO ₂ Na' (—)	566
CH ₃ =CHCl	NaHSO ₃	O ₂	CH ₃ CH ₂ SO ₂ Na (90)	567
CH ₂ =CH ₂ (35–40 p.s.i.)	NH ₄ HSO ₃	O ₂	CH ₃ CH ₂ SO ₂ NH ₄ (12)	210, 217
CH ₂ =CH ₂ (700–1000 atm.)	NaHSO ₃	Peroxide	H(CH ₂ CH ₂) _n SO ₂ Na (—) <i>n</i> = 4 (average)	218
CF ₃ CF=CH ₂	NaHSO ₃	Peroxide	CF ₃ CHFCF ₂ SO ₂ Na (64)	215
CH ₃ CH=CH ₂	NH ₄ HSO ₃	O ₂ or NaNO ₂ + NaNO ₃	CH ₃ CH ₂ CH ₂ SO ₂ NH ₄ (55)	210
HOCH ₂ CH=CH ₂	(NH ₄)KHSO ₃ (pH = 7)	Air	H(OCH ₂) ₃ SO ₂ K (Na) (94–100)	221, 220, 568, 560, 570, 210
(CH ₃) ₂ C=CH ₂	KHSO ₃ (pH = 4) NaHSO ₃	Air O ₂	KO ₂ SCH ₂ CH(SO ₂ K)CH ₂ OH (—) (CH ₃) ₂ CHCH ₂ SO ₂ Na (62)	210

$\text{HOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$	NaHSO_3	O_2	$\text{HO(CH}_2)_3\text{SO}_2\text{Na}$ (almost quant.)	216
$\text{CH}_2\text{CH}=\text{CHCH}_2\text{OH}$	NaHSO_3	O_2	$\text{CH}_2\text{CH(SO}_2\text{Na)CH}_2\text{CH}_2\text{OH}$ (—)	216
$n\text{-C}_6\text{F}_{13}\text{CF}=\text{CF}_2$	NaHSO_3	Peroxide	$n\text{-C}_6\text{F}_{13}\text{CHFCF}_2\text{SO}_2\text{Na}$ (79)	215
C_2H_5	NH_4HSO_3	None added	$\text{C}_2\text{H}_5\text{SO}_2\text{NH}_2$ (86)	217
	NH_4HSO_3	None added	 (57)	217
$n\text{-C}_6\text{H}_{11}\text{CF}=\text{CF}_2$	NaHSO_3	Peroxide	$n\text{-C}_6\text{H}_{11}\text{CHFCF}_2\text{SO}_2\text{Na}$ (73)	215
$\text{C}_6\text{H}_5\text{CH}=\text{CHSO}_2\text{Na}$	NaHSO_3	O_2	$\text{C}_6\text{H}_5\text{CH(SO}_2\text{Na)CH}_2\text{SO}_2\text{Na}$ (—)	224
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	NH_4HSO_3	O_2	$\text{C}_6\text{H}_5\text{CH(OH)CH}_2\text{SO}_2\text{NH}_2$ (50)	214, 210,
			$\text{C}_6\text{H}_5\text{CH}=\text{CHSO}_2\text{NH}_2$ (5)	571
		NaNO_2	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SO}_2\text{NH}_2$ (14)	214
		Peroxide	$\text{C}_6\text{H}_5\text{CH(OH)CH}_2\text{SO}_2\text{Na}$ (16)	
		O_2	$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SO}_2\text{Na}$ (9)	572, 227
		None added	$n\text{-C}_6\text{H}_{11}\text{SO}_2\text{NH}_2$ (87-97)	210, 573
		None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SCH}_2\text{CH}_2\text{SO}_2\text{Na}$ (—)	447, 574,
		None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{S(O)CH}_2\text{CH}_2\text{SO}_2\text{Na}$ (—)	225
		None added	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Na}$ (—)	574, 225
		None added	 (—)	447
		None added	$\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_2\text{Na}$	
		None added	Product not characterized	217
		None added	$\text{C}_{12}\text{H}_{18}\text{N}_2\text{O}_5\text{S}_2$ (—)	217

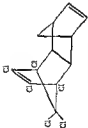
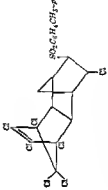






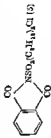
Note: References 385 to 631 are on pp. 371-376.
 † No structure was given for this product.

TABLE X—Continued
N. Addition of Bisulfite to Olefins and Acetylenes—Continued

Olefin	Bisulfite	Catalyst	Products (%)	Refs.
$(CH_3)_2C=CH(CH_2)_7$ $C(CH_3)=CHCH_2OH$ (Goraniol)	$NaHSO_3$	None added	$C_{10}H_{18}SO_7Na_2$ (—)	573
$n-C_4H_9CH=CH_2$ $(CH_3)_2C=CH(CH_2)_5$ $CH(CH_3)CH_2CH_2OH$	NH_4HSO_3 $NaHSO_3$	Peroxide None added	$n-C_{10}H_{18}SO_3NH_4$ (77) $(CH_3)_2CHCH(SO_3Na)(CH_2)_2$ $CH(CH_3)CH_2CH_2OH$ (—)	572, 227 573
 $SO_2CH=CH_2$	$NaHSO_3$	None added	 $SO_2CH_2CH_2SO_3Na$ (—)	447
$n-C_{10}H_{18}Cl=CH_2$ $n-C_{12}H_{24}Cl=CH_2$ $n-C_{12}H_{22}S(O)CH=CH_2$ $n-C_{12}H_{22}SO_2CH=CH_2$ $n-C_{14}H_{28}Cl=CH_2$ $n-C_{16}H_{32}SCH=CH_2$ $n-C_{18}H_{34}S(O)CH=CH_2$ $n-C_{18}H_{32}SO_2CH=CH_2$	NH_4HSO_3 NH_4HSO_3 $NaHSO_3$ $NaHSO_3$ NH_4HSO_3 $NaHSO_3$ $NaHSO_3$ $NaHSO_3$	Peroxide Peroxide None added None added Peroxide None added None added None added	$n-C_{10}H_{18}SO_3NH_4$ (73) $n-C_{12}H_{24}SO_3NH_4$ (60) $n-C_{12}H_{22}S(O)CH_2CH_2SO_3Na$ (—) $n-C_{12}H_{22}SO_2CH_2CH_2SO_3Na$ (—) $n-C_{16}H_{32}SO_3NH_4$ (22) $n-C_{16}H_{32}SCH_2CH_2SO_3Na$ (—) $n-C_{18}H_{34}S(O)CH_2CH_2SO_3Na$ (—) $n-C_{18}H_{32}SO_2CH_2CH_2SO_3Na$ (—)	227, 572 227, 572 447 447, 226 227, 572 447, 574 226, 574 447, 226
Acetylene $HC\equiv CCH_2OH$ $HOCH_2C\equiv CCH_2OH$ $n-C_4H_9C\equiv CH$ $C_6H_5C\equiv CH$ $n-C_4H_9NIICH(CH_3)C\equiv CH$	Bisulfite $KHSO_3$ $NaHSO_3$ $NaHSO_3$ $NaHSO_3$ $NaHSO_3$	Catalyst O_2 None added O_2 O_2 None added	Products (%) $KO_2SCH=C(SO_3K)CH_2OH$ (—) $HOCH_2CH(SO_3Na)CH(SO_3Na)CH_2OH$ (—) $n-C_4H_9CH=CHSO_3Na$ (17) $n-C_4H_9CH(SO_3Na)CH_2SO_3Na$ (32) $C_6H_5CH=CHSO_3Na$ (16) $C_6H_5CH(SO_3Na)CH_2SO_3Na$ (40) $n-C_4H_9NIICH(CH_3)CH(SO_3Na)CH_2SO_3Na$ (—)	Refs. 210, 575 224, 575 224 224 575

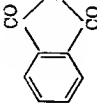
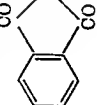
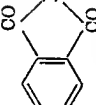
O. Addition of Sulfuryl and Sulfonyl Halides to Olefins

Halide	Olefin	Catalyst	Products (%)	Refs.
SO_2Cl_2	$CH_2=CH_2$ $n-C_4H_9CH=CH_2 + SO_2$	Peroxide Peroxide	$CH(CH_2CH_2)_nSO_2Cl$ $n-C_4H_9CHClCH_2Cl$ (79) $(n-C_4H_9CHClCH_2)_2SO_2$ (13)	238 230

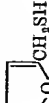

$C_4H_5SO_2I$		Peroxide		149, 232 (39)
$CH_2=CHCN$ $CH_2=C(CH_3)CN$ $CH_2CH=CHCH_3$ (cis or trans) $CH_2=CHCOOC_2H_5$		UV UV UV UV	$C_4H_5SO_2CH_2CHCN$ (78) $C_4H_5SO_2CH_2CH(CH_3)CN$ (98) $C_4H_5SO_2CH_2CH(CH_3)CHICH_3$ (99) $C_4H_5SO_2CH_2CHICOC_2H_5$ (52)	229 228 228, 231 228
$C_4H_5CH=CH_2$		UV		228
$CH_2=CHC_6H_4N$		UV	$C_4H_5SO_2CH_2CHIC_6H_4$ (72)	228
$CH_2=CHC_6H_4Cl$		Peroxide	 	240

Note. References 385 to 631 are on pp. 371-376.

TABLE X—Continued
O. Addition of Sulfuryl and Sulfonyl Halides to Olefins—Continued

Halide	Olefin	Catalyst	Products (%)	Refs.
 NSO_2Cl (contd.)	$\text{CH}_2=\text{CHC}_6\text{H}_{11-n}$	Peroxide	 $\text{NSO}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_{17-1}$ (64)	240
 $\text{NSO}_2(\text{C}_{10}\text{H}_{20})_2\text{Cl}$ (9)				



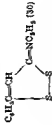
P. Miscellaneous Additions to Form Carbon-Sulfur Bonds

Addendum	Unsaturated	Catalyst	Products (%)	Refs.
Unsaturated Thiols $\text{CH}_2=\text{CHCH}_2\text{SH}$ $\text{CH}_3\text{CH}=\text{CHCH}_2\text{SH}$ $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{SH}$		None added None added None added	$(\text{C}_3\text{H}_5\text{S})_x$ (—) Polymer* (—) Polymer* (—)	117, 116 115 115
 CH_2SH		None added	$(\text{C}_3\text{H}_5\text{OS})_x$ (—)	570
 SH		None added	Polymer* (—)	115
$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{SH}$ $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{SH}$		None added None added	Polymer* (—) Polymer* (80)	115 115
 $\text{CH}_2\text{CH}_2\text{SH}$		$(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{CuSO}_4$	Polymer (63)	118
$\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{SH}$		None added	$(\text{C}_6\text{H}_5\text{S})_x$ (—)	117

$\text{CF}_3\text{Cl}=\text{CF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CF}_2\text{Cl}$ (42)	245
$\text{CH}_2=\text{CF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CFCl}_2$ (12)	245
$\text{CH}_2=\text{CF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CH}_2\text{CF}_2\text{Cl}$ (50)	245
$\text{CH}_2=\text{CHCl}$	UV	$\text{CF}_2\text{SCH}_2\text{CF}_2\text{Cl}$ (11)	245
$\text{CF}_2=\text{CFCF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CH}_2\text{Cl}$ (40)	245
		$\text{CF}_2\text{SCH}_2\text{CF}_2\text{Cl}$ (11)	
		$\text{CF}_2\text{SCH}_2\text{OCH}_2\text{Cl}$ (73)	
		$\text{CF}_2\text{SCH}_2\text{CHCl}_2$ (4)	
		$\text{CF}_2\text{SCF}_2\text{CFClCF}_2$ (16)	
		$\text{CF}_2\text{SCF}_2\text{CF}_2\text{CF}_2\text{Cl}$ (10)	
		$\text{CF}_2\text{SCF}_2\text{CF}_2\text{CF}_2\text{SCF}_2$ (10)	
		$\text{CH}_2\text{CF}_2\text{CF}_2\text{Cl}$ (20)	
		CF_2SSCF_2 (—)	
		$\text{CH}_2\text{OCF}_2\text{SCF}_2\text{CF}_2\text{Cl}$ (16)	
		$\text{CH}_2\text{OCF}_2\text{CF}_2\text{SCF}_2$ (26)	
		$\text{CH}_2\text{OCF}_2\text{CF}_2\text{Cl}$ (31)	
		$\text{CH}_2\text{OCF}_2\text{SCF}_2\text{CF}_2\text{SCF}_2$ (11)	
		CF_2SSCF_2 (—)	
		1:1 adduct (59)	
			245
			243
			244
			243
			243, 244
			243
			244

$\text{CF}_3\text{Cl}=\text{CF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CF}_2\text{Cl}$ (42)	245
$\text{CH}_2=\text{CF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CFCl}_2$ (12)	245
$\text{CH}_2=\text{CF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CH}_2\text{CF}_2\text{Cl}$ (50)	245
$\text{CH}_2=\text{CHCl}$	UV	$\text{CF}_2\text{SCH}_2\text{CF}_2\text{Cl}$ (11)	245
$\text{CF}_2=\text{CFCF}_2$	UV	$\text{CF}_2\text{SCF}_2\text{CH}_2\text{Cl}$ (40)	245
		$\text{CF}_2\text{SCH}_2\text{CF}_2\text{Cl}$ (11)	
		$\text{CF}_2\text{SCH}_2\text{OCH}_2\text{Cl}$ (73)	
		$\text{CF}_2\text{SCH}_2\text{CHCl}_2$ (4)	
		$\text{CF}_2\text{SCF}_2\text{CFClCF}_2$ (16)	
		$\text{CF}_2\text{SCF}_2\text{CF}_2\text{CF}_2\text{Cl}$ (10)	
		$\text{CF}_2\text{SCF}_2\text{CF}_2\text{CF}_2\text{SCF}_2$ (10)	
		$\text{CH}_2\text{CF}_2\text{CF}_2\text{Cl}$ (20)	
		CF_2SSCF_2 (—)	
		$\text{CH}_2\text{OCF}_2\text{SCF}_2\text{CF}_2\text{Cl}$ (16)	
		$\text{CH}_2\text{OCF}_2\text{CF}_2\text{SCF}_2$ (26)	
		$\text{CH}_2\text{OCF}_2\text{CF}_2\text{Cl}$ (31)	
		$\text{CH}_2\text{OCF}_2\text{SCF}_2\text{CF}_2\text{SCF}_2$ (11)	
		CF_2SSCF_2 (—)	
		1:1 adduct (59)	
			245
			243
			244
			243
			243, 244
			243
			244

As in reference 345 to 431 are on pp. 371-376.
 * No structure was given for this product.
 * The polymer was not characterized.

<i>Durel/solite</i> H_2S_2	$CH_2=CHC_3H_7$, n	None added	H_2S (5) $(C_2H_5)_2S$ (21) $(C_2H_5)_2S_2$ (12) $(C_2H_5)_2S_3$ (25) H_2S (21) $(C_2H_5)_2S$ (15) $(C_2H_5)_2S_2$ (3) $(C_2H_5)_2S_3$ (19) S (16)	255, 254
	$CH_3CH=CHC_3H_7$	None added		255
		None added	H_2S (30)  $(\text{cyclohexyl})_2S_2$ (7) $C_4H_9C=CH$  UV	255
CH_3AsCH_3 ($\approx C_4H_9$) S_2	$CF_3=CF_2$ $CH_3CO_2CH=CH_2$	Iodine UV	CH_3SCF_3 , CF_3SCH_3 , (—) $CH_3CO_2CH(SC_2H_5)_2CH_2SC_2H_5$, n (30)	278 27 76

Notes: References 285 to 331 are on pp. 271-372.
* No structure was given for this product.

TABLE XI

ADDITION OF SILANES TO OLEFINS AND ACETYLENES

A. *Trichlorosilane and Olefins*

	Catalyst	Products (%)	Refs.
Olefin	Peroxide	(C ₂ H ₅ Cl) ₂ SiCl ₂ (38)	266
	UV	CH ₃ CF ₂ SiCl ₂ (45)	281
	UV	(C ₂ H ₅ Cl) ₂ SiCl ₂ (19)	266
	Thermal (~200°)	CH ₃ CF ₂ SiCl ₂ (—)	279, 280
	Ozone	CH ₃ CF ₂ SiCl ₂ (—)	270
	Thermal (450°)	(C ₂ H ₅ Cl) ₂ SiCl ₂ (30)	279
	Thermal (450°)	CFCl=CFSiCl ₂ (—)	280
	UV	CHCl ₂ CCl ₂ SiCl ₂ (1)	297
	Peroxide	CCl ₂ =CCSiCl ₂ (7)	297
	Thermal (300–600°)	CHCl ₂ CCl ₂ SiCl ₂ (2–5)	297, 294
	UV	CCl ₂ =CCSiCl ₂ (11–13)	277
	Thermal (200°)	CH ₃ CF ₂ SiCl ₂ (14–58) + higher telomers	279
	Ozone	CH ₃ CF ₂ SiCl ₂ (—)	270
	Thermal (500°)	CCl ₂ =CCSiCl ₂ (40)	295, 296
	UV	CH ₃ CF ₂ SiCl ₂ (50)	281
	Thermal (400°)	CHCl=CHSiCl ₂ (25)	296
	γ-Rays	CH ₂ CHClCHSiCl ₂ (27)	260
	Thermal (550°)	CH ₂ CHClCHSiCl ₂ (12)	295
	Thermal (600°)	(C ₂ H ₅ Cl) ₂ SiCl ₂ (—)	272
	Peroxide	CH ₃ CF ₂ SiCl ₂ (53)	297, 570
	Thermal (300°)	Cl ₂ SiCl ₂ CH ₂ SiCl ₂ (10)	580
	Peroxide	Cl ₂ SiCl ₂ CH ₂ SiCl ₂ (—)	581
	Azo	C ₂ H ₅ SiCl ₂ (—)	274, 278,
	Thermal (285°)	11(C ₂ H ₅) ₂ SiCl ₂	275, 292,
		n = 1 (20)	582, 583
		n = 2 (25)	
		n = 3 (15)	
		n = 4 (13)	
		n = 5 (4)	
		n > 5 (12)	

	Azob/High pressure		
$\text{CF}_3\text{CH}=\text{OCH}_3$		$\text{H}(\text{C}_2\text{H}_5)_2\text{SnCl}_2$	261
$\text{CF}_3\text{CF}=\text{CF}_2$		$n = 1$ (13)*	
		$n = 2$ (9)	
		$n = 3$ (4)	
		$n > 3$ (33)	
$\text{CF}_3\text{CH}=\text{CH}_2$		$\text{CF}_3\text{CH}_2\text{CH}_2-\text{SnCl}_2$ (9)	266
$\text{CH}_3\text{C}(\text{CH}_3)=\text{CH}_2$		$\text{CF}_3\text{CH}_2\text{CH}_2-\text{SnCl}_2$ (24)	266
		$\text{CF}_3\text{CHFCF}_2\text{SnCl}_2$ (4)	266
		$\text{CF}_3\text{CHFCF}_2\text{SnCl}_2$ (4)	266
		$\text{CF}_3\text{CH}_2\text{CH}_2\text{SnCl}_2$ (72-91)	279
		$\text{CF}_3\text{CH}_2\text{CH}_2\text{SnCl}_2$ (75)	266, 269
		$\text{ClCH}_2\text{CH}_2\text{SnCl}_2$ (9)	266
		$\text{ClCH}_2\text{CH}_2\text{SnCl}_2$ (20)	259
		$\text{ClCH}_2\text{CH}_2\text{SnCl}_2$ (40)	259
		$\text{H}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{SnCl}_2$ (24)	260
		$\text{Cl}_2\text{Sn}(\text{CH}_2)_2\text{SnCl}_2$ (23-62)	257, 279
$\text{Cl}_2\text{S}(\text{CH}_2)_2\text{CH}_2$		$n = \text{C}_2\text{H}_5\text{SnCl}_2$ (63-90)	293
$\text{CH}_3\text{CH}=\text{CH}_2$		$\text{C}_2\text{H}_5\text{CHFCF}_2\text{SnCl}_2$ (—)	583, 292
$\text{CH}_3\text{CF}=\text{CF}_2$		$\text{CF}_3-\text{CFCHFCF}_2\text{SnCl}_2$ (—)	279
$\text{CF}_3\text{CF}=\text{CF}_2$		$\text{C}_2\text{H}_5\text{CHFCF}_2\text{SnCl}_2$ (29)	279, 290
		$\text{C}_2\text{H}_5\text{CHFCF}_2\text{SnCl}_2$ (22)	266
		$\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{SnCl}_2$ (40)	266
		$\text{NO}(\text{CH}_2)_2\text{SnCl}_2$ (8)	260
		$\text{H}(\text{C}_2\text{H}_5)_2\text{SnCl}_2$ (—)	291
		$\text{CH}_3-\text{CH}(\text{CH}_3)_2\text{SnCl}_2$ (—)	258
		$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{SnCl}_2$ (10)	284
		$n = \text{C}_2\text{H}_5\text{SnCl}_2$ (61)	292, 283
		$(\text{CH}_3)_2\text{CHCH}_2\text{SnCl}_2$ (73-82)	292, 283
		$(\text{CH}_3)_2\text{CHCH}_2\text{SnCl}_2$ (4-11)	292, 283
		$(\text{CH}_3)_2\text{CHCH}_2\text{SnCl}_2$ (5)	257, 281
		$\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{SnCl}_2$ (93)	259
		$\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{SnCl}_2$ (64)	260
		$\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{SnCl}_2$ (93)	583, 292
		$\text{CH}_3\text{O}(\text{CH}_2)_2\text{SnCl}_2$ (—)	260
		$\text{C}_2\text{H}_5\text{O}(\text{CH}_2)_2\text{SnCl}_2$ (53)	585

Note. References 385 to 631 are on pp. 371-376.
 * The figures are facts by weight, not percentages.

TABLE XI—Continued








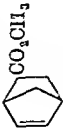












A. Trichlorosilane and Olefins—Continued		Products (%)	Refs.
Olefin	Catalyst		
$C_3F_5CH=CH_2$	γ -Rays	$C_3F_5CH_2CH_2SiCl_3$ (52)	260
$C_3F_5C(CH_3)=CH_2$	γ -Rays	$C_2F_5CH(CH_3)CH_2SiCl_3$ (9)	260
	Thermal (280°)	Cl_3Si  $SiCl_3$ (45)	586
	Thermal (280°)	 $SiCl_3$ (59)	292
	γ -Rays	$SiCl_3$ (96)	260
$CH_3CO_2CH_2CH=CH_2$	γ -Rays	$CH_3CO_2(CH_2)_2SiCl_3$ (22) $H(CH_3CO_2CH_2)_2SiCl_3$ (71)	260
$C_2H_5CH=CH_2$	Peroxide	$n-C_2H_5SiCl_3$ (0-100)†	263
	Thermal (250°)	$n-C_2H_5SiCl_3$ (76)	292
	Peroxide	$n-C_2H_5SiCl_3$ (44)	257, 581
	Thermal (290°)	$n-C_2H_5CH(CH_3)SiCl_3$ (70)	292, 582
	Peroxide	$n-C_2H_5CH(CH_3)SiCl_3$ (70:30)†	263
$C_2H_5CH=CHCH_3$	Peroxide	$C_2H_5CH(C_2H_5)SiCl_3$ (5-11)	587
	Peroxide	$(CH_3)_2CHCH_2CH_2SiCl_3$ (26)	259
$(CH_3)_2C=CHCH_3$	Peroxide	$(CH_3)_2CHCH(CH_3)SiCl_3$ (78)	292
	Thermal (280°)	$C_3H_7SiCl_3$ (64)	259
	UV	$C_3H_7SiCl_3$ (94)	260
	γ -Rays	$C_2H_5O(CH_2)_2SiCl_3$ (84)	585
$C_4H_9OCH_2CH=CH_2$	Peroxide	$(CH_3)_2SiCH_2CH_2SiCl_3$ (70-90)	588, 287
$C_3F_5C(CH_3)=CH_2$	γ -Rays	$C_3F_5CH(CH_3)CH_2SiCl_3$ (11)	260
	Thermal (280°)	cyclo- $C_6H_{11}SiCl_3$ (45)	586

TABLE XI—Continued

A. Trichlorosilane and Olefins—Continued

Catalyst	Products (%)	Refs.
Olefin		
$C_6H_5CH=CH_2$	$H(C_2H_5)_2SiCl_3$ $C_6H_5SiCl_3$ (30) $H(C_2H_5)_2SiCl_3$ (7) $H(C_2H_5)_3SiCl_3$ (>80) (average value of $n = 59$)	261 582 589
	 $SiCl_3$ (21)	258, 590
$n-C_6H_{13}CH=CH_2$	$n-C_6H_{17}SiCl_3$ (99) $n-C_6H_{17}SiCl_3$ (31-47) $n-C_6H_{17}SiCl_3$ (80-94) $n-C_6H_{17}SiCl_3$ (75) $n-C_6H_{17}SiCl_3$ (99) $C_6H_{17}SiCl_3$ (99) $n-C_6H_{17}CH(CH_3)CH_2SiCl_3$ (70) $(CH_3)_3CCH_2CH(CH_3)CH_2SiCl_3$ (9) $(CH_3)_3CCH_2CH(CH_3)CH_2SiCl_3$ (30) $(CH_3)_3CCH_2CH(CH_3)CH_2SiCl_3$ (7) $(CH_3)_3C=CHSiCl_3$ (36) $(CH_3)_3CCH(CH_2H_7)SiCl_3$ (18) $C_6H_{17}SiCl_3$ (9) $(CH_3)_3CCH(CH_2H_7)SiCl_3$ (—) $(C_2H_5)_3SiCH_2CH_2SiCl_3$ (42)	256, 259 259 583, 292 261 260 259 259 259 261 292
$(CH_3)_3CCH=C(CH_3)_2$ $(C_2H_5)_3SiCH=CH_2$	$(CH_3)_3CCH=C(CH_3)_2$ $(C_2H_5)_3SiCH=CH_2$	259 258 588
	Cl_3Si  CO_2CH_3 (—)	591
$n-C_7H_{15}CH=CH_2$	$n-C_9H_{19}SiCl_3$ (89) $n-C_9H_{19}SiCl_3$ (61)	292 587

$(C_2H_5)_3Si(CH_2)_2SiCl_3$				293
	Peroxide		$(C_2H_5)_3Si(CH_2)_2SiCl_3$ (10)	556
$CH_2=CH(CH_2)_3CH_2SiCl_3$	Thermal (280°)		$CH_2=CH(CH_2)_3CH_2SiCl_3$ (—)	592
$C_4H_9Si(CH_2)_3CH=CH_2$	UV		$C_4H_9Si(CH_2)_3CH_2SiCl_3$ (24)	598
$C_4H_9Si(CH_2)_3CH=CH_2$	Peroxide		$CH_2=CH(CH_2)_3$ (68)	546
$CH_2=C(CH_3)C(CH_3)=CH_2$	Thermal (280°)		$CH_2=CH(CH_2)_3CH_2SiCl_3$ (20)	
	UV		$CH_2=CH(CH_2)_3CH_2SiCl_3$ (—)	592
	Peroxide		$CH_2=CH(CH_2)_3CH_2SiCl_3$ (38)	599
	Peroxide		$CH_2=CH(CH_2)_3$ (49)	599, 593, 301, 302
	UV		$CH_2=CH(CH_2)_3$ (—)	300

Note. References 385 to 631 are on pp. 371-376.

TABLE XI—Continued
A. Trichlorosilane and Olefins—Continued

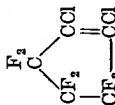
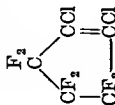
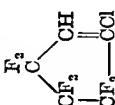
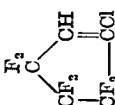


Olefin	Catalyst	Products (%)	Refs.
	$\text{C}_{10}\text{H}_{17}\text{SiCl}_3$ (56)		299
	$\text{C}_{10}\text{H}_{17}\text{SiCl}_3$ (22)		299
$n\text{-C}_8\text{H}_{17}, \text{CH}=\text{CH}_2$	$\text{C}_{10}\text{H}_{17}\text{SiCl}_3$ (69)		292
$\text{CH}_3=\text{CH}(\text{CH}_2)_4\text{COCl}$	$n\text{-C}_{10}\text{H}_{17}, \text{SiCl}_3$ (60-90)		583, 292
$n\text{-C}_{11}\text{H}_{23}, \text{CH}=\text{CH}_2$	$n\text{-C}_{10}\text{H}_{17}, \text{SiCl}_3$ (63)		587
$\text{CH}_3=\text{CH}(\text{CH}_2)_4\text{COCl}$	$\text{C}_{12}\text{Si}(\text{CH}_3)_2\text{COCl}$ (—)		594
$\text{CH}_3=\text{CH}(\text{CH}_2)_4\text{CO}_2\text{CH}_3$	$\text{C}_{12}\text{H}_5\text{Si}(\text{CH}_3)_2(\text{CH}_2)_3\text{SiCl}_3$ (22)		293
$n\text{-C}_{10}\text{H}_{17}, \text{CH}=\text{CH}_2$	$\text{C}_{12}\text{Si}(\text{CH}_3)_2\text{CO}_2\text{CH}_3$ (—)		595
$[(\text{CH}_3)_3\text{CCl}_2]_2\text{C}=\text{CH}_2$	$n\text{-C}_{12}\text{H}_{25}, \text{SiCl}_3$ (84-95)		583, 292
	$\text{C}_{12}\text{H}_{25}, \text{SiCl}_3$ (2)		269
	Cl_3Si $\text{CO}_2\text{C}_2\text{H}_5$ $\text{CO}_2\text{C}_2\text{H}_5$ (—)		591
$n\text{-C}_{13}\text{H}_{27}, \text{CH}=\text{CH}_2$	$n\text{-C}_{12}\text{H}_{25}, \text{SiCl}_3$ (88)		292, 583
$n\text{-C}_{11}\text{H}_{23}, \text{Si}(\text{CH}_3)_2\text{SiCl}_3$ (13)	$(n\text{-C}_{11}\text{H}_{23})_2\text{Si}(\text{CH}_3)_2\text{SiCl}_3$ (13)		293
$n\text{-C}_{11}\text{H}_{23}, \text{CH}=\text{CH}_2$	$n\text{-C}_{10}\text{H}_{19}, \text{SiCl}_3$ (93)		292, 268
$n\text{-C}_{12}\text{H}_{25}, \text{SiCl}_3$ (30)	$n\text{-C}_{12}\text{H}_{25}, \text{SiCl}_3$ (30)		587
$n\text{-C}_{12}\text{H}_{25}, \text{CH}=\text{CH}_2$	$n\text{-C}_{12}\text{H}_{25}, \text{SiCl}_3$ (88-94)		258, 583
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2$	$n\text{-C}_{12}\text{H}_{25}, \text{SiCl}_3$ (98)		261
	$\text{C}_{12}\text{H}_{25}, \text{O}_2\text{SiCl}_3$ (22)		596
$n\text{-C}_{13}\text{H}_{27}, \text{CH}=\text{CH}_2$			
$n\text{-C}_{11}\text{H}_{23}, \text{Si}(\text{CH}_3)_2\text{SiCl}_3$			
$n\text{-C}_{11}\text{H}_{23}, \text{CH}=\text{CH}_2$			
$n\text{-C}_{12}\text{H}_{25}, \text{CH}=\text{CH}_2$			
$\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_3\text{CO}_2\text{CH}_3$			




H. Methylchlorosilane and Olefins

Olefin	Catalyst	Products (%)	Ref.
$\text{CF}_2=\text{CFCl}$	Thermal (440-450°)	$\text{CF}_2-\text{CFSi}(\text{CH}_3)_2\text{Cl}$ (1)	279, 280
$\text{CFCl}=\text{CFCl}$	Thermal (440-450°)	$\text{CFCl}-\text{CFSi}(\text{CH}_3)_2\text{Cl}$ (-)	280
$\text{CF}_2=\text{CCl}_2$	Thermal (450-500°)	$\text{CF}_2\text{Cl}-\text{CFSi}(\text{CH}_3)_2\text{Cl}$ (-)	279
$\text{CCl}_2=\text{CCl}_2$	Thermal (300°)	$\text{CCl}_2-\text{CClSi}(\text{CH}_3)_2\text{Cl}$ (-)	284
$\text{CF}_2=\text{CF}_2$	Peroxide	$\text{CF}_2-\text{CFSi}(\text{CH}_3)_2\text{Cl}$ (6-19)	277
$\text{CH}_2=\text{CHCl}$	UV	$\text{CH}_2\text{Cl}-\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (94)	264
$\text{CH}_2=\text{CHCl}$	Thermal (350-600°)	$\text{CHCl}-\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (20)	272, 277
$\text{CH}_2=\text{CHCl}$	Thermal (350-600°)	$\text{CH}_2-\text{CHSi}(\text{CH}_3)_2\text{Cl}$ (22-39)	279
$\text{CH}_2=\text{CH}_2$	Peroxide	$\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (-)	276, 277, 278
$\text{CH}_2=\text{CH}_2$	Thermal (200°)	$\text{H}(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ n = 1 (24) n = 2 (26) n = 3 (33) n = 4 (23) n = 5 (3) n = 6 (1) n > 6 (3)	276, 277, 278
$\text{CF}_3\text{OCCl}=\text{CCl}_2$	Thermal (300°)	$\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{Cl}$ (-)	294
$\text{CF}_3\text{OCCl}=\text{CF}_2$	$\text{Fe}(\text{CO})_5$	$\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{Cl}$ (70)	264
$\text{CICH}_2\text{CH}=\text{CH}_2$	Peroxide	$\text{CF}_3(\text{C}_6\text{H}_5)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (12)	266
$\text{CF}_3\text{CH}=\text{CH}_2$	Thermal (470-480°)	$\text{CF}_3\text{CF}_2-\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (1)	280
$\text{CF}_3\text{CH}=\text{CH}_2$	γ Rays	$\text{CF}_3\text{CH}=\text{CFSi}(\text{CH}_3)_2\text{Cl}$ (-)	260
$\text{CF}_3\text{CH}=\text{CH}_2$	UV	$\text{H}(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (4)	260
$\text{CH}_2\text{CH}=\text{CH}_2$	Peroxide	$\text{CF}_3\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (11)	269, 260
$\text{CH}_2\text{CH}=\text{CH}_2$	Thermal (300°)	$\text{CF}_3\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (92)	266
$\text{CH}_2\text{CH}=\text{CH}_2$	Thermal (200°)	n-C ₄ H ₉ Si(CH ₃) ₂ Cl (70)	258
		$\text{H}(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (72)	276, 277, 278
		n = 1 (94) n = 2 (28) n = 3 (4)	272
$\text{CH}_2\text{SiCl}_2\text{CH}=\text{CH}_2$	$\text{Fe}(\text{CO})_5$	n-C ₄ H ₉ Si(CH ₃) ₂ Cl (70)	261
$\text{C}_6\text{F}_5\text{CF}=\text{CH}_2$	Thermal (300°)	$\text{ClCH}_2\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (-)	260
	UV	$\text{C}_6\text{F}_5\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (9)	266
	Peroxide	$\text{C}_6\text{F}_5\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}$ (46)	266

Note. References 385 to 431 are on pp. 371-378.

TABLE XI—Continued
B. Methylchlorosilane and Olefins—Continued


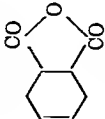
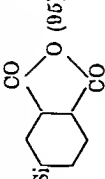
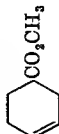



Olefin	Catalyst	Products (%)	Refs.
$\text{CF}_3\text{C}(\text{CH}_3)=\text{CH}_2$	UV	$\text{CF}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ (63)	269
$\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$	Thermal (300°)	$n\text{-C}_2\text{H}_5\text{Si}(\text{CH}_3)\text{Cl}_2$ (—)	258
$\text{CH}_3\text{CH}=\text{CHCH}_3$	γ -Rays	$\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{Si}(\text{CH}_3)\text{Cl}_2$ (57)	260
$\text{Cl}_2(\text{CH}_3)\text{SiCH}_2\text{CH}=\text{CH}_2$	Thermal (280°)	$\text{Cl}_2(\text{CH}_3)\text{Si}(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$ (—)	580
	Thermal (470–500°)	 (—)	279, 280
	Thermal (490–500°)	 (—)	280
$n\text{-C}_3\text{F}_7\text{CH}=\text{CH}_2$	γ -Rays	$\text{C}_3\text{F}_7(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$ (23)	260
$\text{C}_2\text{F}_5\text{C}(\text{CH}_3)=\text{CH}_2$	UV	$\text{C}_2\text{F}_7(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$ (73)	269
	γ -Rays	$\text{C}_2\text{F}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ (2)	260
	γ -Rays	$\text{C}_3\text{H}_7\text{Si}(\text{CH}_3)\text{Cl}_2$ (20)	260
$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$	γ -Rays	$\text{CH}_3\text{CO}_2(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$ (47)	260
$n\text{-C}_6\text{H}_{11}\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_6\text{H}_{11}\text{Si}(\text{CH}_3)\text{Cl}_2$ (10)	257, 581
	Thermal (300°)	$n\text{-C}_6\text{H}_{11}\text{Si}(\text{CH}_3)\text{Cl}_2$ (—)	258
$\text{C}_2\text{H}_5\text{CH}=\text{CHCH}_3$	Peroxide	$n\text{-C}_2\text{H}_5\text{CH}(\text{CH}_3)\text{Si}(\text{CH}_3)\text{Cl}_2$ (21)	257, 581
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	γ -Rays	$(\text{CH}_3)_2\text{CHCH}(\text{CH}_3)\text{Si}(\text{CH}_3)\text{Cl}_2$ (30)	260
$(\text{CH}_3)_3\text{SiCH}=\text{CH}_2$	Peroxide	$(\text{CH}_3)_3\text{Si}(\text{CH}_2)_2\text{Si}(\text{CH}_3)\text{Cl}_2$ (74)	287
	Thermal (300°)	$\text{C}_6\text{H}_{11}\text{Si}(\text{CH}_3)\text{Cl}_2$ (—)	258
	γ -Rays	$\text{C}_6\text{H}_{11}\text{Si}(\text{CH}_3)\text{Cl}_2$ (46)	260







$n\text{-C}_4\text{F}_7\text{C}(\text{CH}_3)=\text{CH}_2$ $n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$ $n\text{-C}_4\text{H}_9\text{CH}=\text{CHCH}_3$ $n\text{-C}_7\text{H}_{15}\text{CH}=\text{CH}_2$	γ -Rays γ -Rays Thermal Peroxide	$\text{C}_2\text{F}_5\text{CH}(\text{CH}_3)\text{CH}_2\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (6) $n\text{-C}_4\text{H}_9\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (55) $\text{C}_2\text{H}_5\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (—) $n\text{-C}_7\text{H}_{15}\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (21)	260 260 598 587
 $n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$\text{Cl}_3(\text{CH}_2)_3\text{Si}-\text{Cyclohexyl}-\text{CO}_2\text{CH}_3$	591
$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_{10}\text{H}_{19}\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (38)	587
	Peroxide	$\text{C}_{10}\text{H}_{17}\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (32)	299
	Peroxide	$\text{C}_{10}\text{H}_{17}\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (18)	209
$n\text{-C}_{11}\text{H}_{21}\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_{11}\text{H}_{21}\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (—)	258

Silane	Olefin	Catalyst	Product (%)	Refs.
SiH_4	$\text{CH}_2=\text{CH}_2$ $\text{CH}_2=\text{CH}_2$	Thermal (75–200°) Thermal (150–510°)	$\text{C}_2\text{H}_5\text{SiH}_2$ (—) $\text{H}(\text{C}_2\text{H}_5)_2\text{SiH}_2$ ($n = 1, 2, \text{etc.}$) and $(\text{C}_2\text{H}_5)_3\text{SiH}_{3-n}$ ($n = 1, 2, 3, 4$)	286 271
	$\text{CH}_2=\text{CH}_2$	UV/flow system	$\text{C}_2\text{H}_5\text{SiH}_2$ (3) $n\text{-C}_4\text{H}_9\text{SiH}_2$ (4) $\text{C}_2\text{H}_5(\text{SiH}_2)_2$ (5) $\text{C}_2\text{H}_5\text{SiH}_2$ (—) $(\text{C}_2\text{H}_5)_2\text{Si}$ (—) $(\text{C}_2\text{H}_5)_2\text{Si}(\text{Cl})\text{SiCl}$ (—) $(\text{C}_2\text{H}_5)_2\text{SiH}_2$ (30) $(\text{C}_2\text{H}_5)_2\text{SiH}$ (7) $(\text{C}_2\text{H}_5)_3\text{Si}$ (2) $n\text{-C}_{11}\text{H}_{21}\text{Si}(\text{C}_2\text{H}_5)_2\text{H}_2$ (60)	271 599, 286 599, 286 270 286
$\text{C}_2\text{H}_5\text{SiH}_2$ $\text{C}_2\text{H}_5\text{SiH}_2$	$\text{CH}_2\text{CH}=\text{CH}_2$ $(\text{CH}_3)_2\text{C}=\text{CH}_2$ $\text{CF}_3=\text{CFCF}_3$ $\text{CH}_2=\text{CH}_2$	Thermal (75–200°) Thermal (100°) Ozone Thermal (315°)		
$n\text{-C}_{11}\text{H}_{21}\text{SiH}_2$	$n\text{-C}_{11}\text{H}_{21}\text{CH}=\text{CH}_2$	Peroxide		278

Note. References 385 to 631 are on pp. 371–376.

TABLE XI—Continued
C. Silane and Other Substituted Silanes and Olefins—Continued

Silane	Olefin	Catalyst	Products (%)	Refs.
$C_6H_5SiH_3$	$CH_3CO_2CH_2CH=CH_2$	Peroxido	$CH_3CO_2(CH_2)_3Si(C_6H_5)_2H_2$ (72-77)	278, 600
		Peroxido	$C_6H_{11}Si(C_6H_5)_2H_2$ (25)	278
	$(CH_2=CHCH_2)_2O$ $(CH_3)_3SiOCH_2CH=CH_2$ $(CH_3COO)CHCH=CH_2$ $(C_2H_5O)_2CHCH=CH_2$	Peroxido Peroxido Peroxido Peroxido	$CH_2=CHCH_2O(CH_2)_3Si(C_6H_5)_2H_2$ (60) $(CH_3)_3SiO(CH_2)_3Si(C_6H_5)_2H_2$ (—) $(CH_3COO)CH(CH_2)_3Si(C_6H_5)_2H_2$ (38) $(C_2H_5O)_2CH(CH_2)_3Si(C_6H_5)_2H_2$ (55)	278 278, 600 278 278
		Peroxido	$H_2(C_6H_5)_2Si$  (95)	278
		Peroxido	$H_2(C_6H_5)_2Si$  (66)	591, 278
	$n-C_6H_{13}CH=CH_2$	Peroxido	$n-C_6H_{17}Si(C_6H_5)_2H_2$ § $(n-C_6H_{17})_2Si(C_6H_5)_2H$ $(n-C_6H_{17})_2SiC_6H_5$ $[(CH_3)_3Si]_2N(CH_2)_3Si(C_6H_5)_2H_2$ (81) $o-CH_3CO_2C_6H_4(CH_2)_3Si(C_6H_5)_2H_2$ (50) $CH_3O_2C(CH_2)_8Si(C_6H_5)_2H_2$ (98)	278 601, 278 278 591
		Peroxido	CH_3CO_2  -Si(C_6H_5)_2H_2 (79)	600, 278
	$CH_3CO_2(CH_2)_6CH=CH_2$ $(CH_3)_3SiNH(CH_2)_6CH=CH_2$ $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_3$	Peroxido Peroxido Peroxido	$CH_3CO_2(CH_2)_6Si(C_6H_5)_2H_2$ (—) $(CH_3)_3SiNH(CH_2)_6Si(C_6H_5)_2H_2$ (—) $C_{17}H_{33}(CO_2CH_3)Si(C_6H_5)_2H_2$ (100)	600 601 591, 278


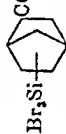

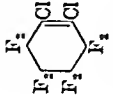

$\text{ClC}_6\text{H}_4\text{SiH}_3$		Peroxide		601
Cl_2SiH_2	$\text{CCl}_2=\text{CCl}_2$ $\text{CF}_2=\text{CF}_2$ $\text{CF}_2\text{CF}=\text{CF}_2$ $\text{CF}_3\text{CH}=\text{CH}_2$	Thermal (300°) Thermal (200°) Thermal (200°) UV	$(\text{CCl}_2=\text{CCl}_2)_2\text{SiCl}_2$ (—) $(\text{CHF}_2\text{CF}_2)_2\text{SiCl}_2$ (—) $(\text{CF}_3\text{CHFCF}_3)_2\text{SiCl}_2$ (—) $\text{CF}_3\text{CH}_2\text{CH}_2\text{SiHCl}_2$ (9-83) $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiCl}_2$ (77-0) $\text{CH}_2\text{CF}_2\text{CF}_2\text{Si}(\text{CH}_3)_2\text{H}$ (54-83) $\text{H}(\text{CF}_3)_2\text{Si}(\text{CH}_3)_2\text{H}$ (7-20) $(\text{CHF}_2\text{CF}_2)_2\text{Si}(\text{CH}_3)_2$ (2-6) $\text{H}(\text{CF}_3)_2\text{Si}(\text{C}_6\text{H}_4)_2\text{N}(\text{CH}_3)_2$ (0-8) $\text{CH}_3\text{O}_2\text{C}(\text{CH}_3)_2\text{Si}(\text{C}_6\text{H}_4)_2(\text{CH}_2)_2\text{H}$ (43)	294 279 279 269 267
$(\text{CH}_3)_3\text{SiH}_4$	$\text{CF}_3=\text{CF}_3$	UV		278
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiH}_2$	$\text{CH}_3\text{O}_2\text{CCH}_2\text{CH}=\text{CH}_2$	Peroxide		278
$(\text{C}_6\text{H}_5)_2\text{SiH}_2$		Peroxide		602 258, 583 587 600 601
Br_2SiH_2	$n\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ $\text{CH}_2\text{CH}=\text{CH}_2$ $(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$ $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$ $(\text{CH}_3)_2\text{NCH}_2\text{CH}=\text{CH}_2$	Peroxide Thermal (225-250°) Peroxide Peroxide Peroxide	$n\text{C}_6\text{H}_5\text{Si}(\text{C}_6\text{H}_5)_2\text{H}$ (41) $n\text{C}_6\text{H}_5\text{SiBr}_2$ (76) $(\text{CH}_3)_2\text{CH}(\text{CH}_3)_2\text{SiBr}_2$ (9) $\text{CH}_3\text{CO}_2(\text{CH}_3)_2\text{SiBr}_2$ (—) $(\text{CH}_3)_2\text{N}(\text{CH}_3)_2\text{SiBr}_2$ (—)	288 288, 289 289
		Peroxide	$\text{C}_6\text{H}_5\text{SiBr}_2$ (28)	
		UV UV	$\text{C}_6\text{H}_5\text{SiBr}_2$ (70) $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiBr}_2$ (70)	

Note - References 385 to 631 are on pp 371-376.

§ The relative amounts of products are dependent on the ratio of reactants

TABLE XI—Continued

C. Silane and Other Substituted Silanes and Olefins—Continued

Silane	Olefin	Catalyst	Products (%)	Refs.
Br_3SiH (contd.)	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$ $n\text{-C}_3\text{H}_7\text{CH}=\text{CH}_2$	UV UV	$n\text{-C}_4\text{H}_9\text{SiBr}_2$ (71) $n\text{-C}_3\text{H}_7\text{SiBr}_2$ (75)	603 289
		Peroxide	 (82)	278
$\text{CH}_3(\text{SiHCl}_2)_2$ $\text{Cl}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{H}$	$n\text{-C}_7\text{H}_{15}\text{CH}=\text{CH}_2$ $n\text{-C}_6\text{H}_{13}\text{CH}=\text{CH}_2$ $n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$ $\text{CH}_3\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide Peroxide Peroxide Peroxide	$n\text{-C}_7\text{H}_{15}\text{SiBr}_2$ (79) $n\text{-C}_6\text{H}_{13}\text{SiBr}_2$ (74) $\text{CH}_3\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ (22) $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ (10)	587 587 289 584
		Peroxide	$\text{C}_6\text{H}_{11}\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ (11)	288
$\text{Cl}_2\text{Si}(\text{C}_2\text{H}_5)_2\text{H}$ $\text{Cl}_2(n\text{-C}_4\text{H}_9)_2\text{SiH}$	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_3)_2\text{CH}=\text{CH}_2$ $\text{Cl}_2(\text{C}_2\text{H}_5)_2\text{SiCH}=\text{CH}_2$ $\text{CH}_2=\text{CH}_2$	UV Thermal (300°) Thermal (300°)	$\text{CH}_3\text{O}_2\text{C}(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ (32) $\text{Cl}_2(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ (—) $n\text{-C}_4\text{H}_9\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ + high-boiling material (25) $(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiCl}_2$ (85)	604 580 582
$\text{Cl}_2(\text{CF}_3\text{CH}_2\text{CH}_2)_2\text{SiH}$	$\text{CF}_3\text{CH}=\text{CH}_2$	UV		269
$\text{Cl}_2(\text{C}_6\text{H}_5)_2\text{SiH}$		Thermal (400–500°)	 (—)	280
	$\text{CH}_2=\text{CHCl}$ $\text{CH}_2=\text{CH}_2$	Thermal (550°) Thermal (290°)	$\text{CH}_2=\text{CHSi}(\text{C}_6\text{H}_5)_2\text{Cl}_2$ (—) $\text{H}(\text{C}_6\text{H}_5)_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}_2$ (—) (n = 1, 2, 3)	272 605, 273
	$\text{CH}_3\text{CH}=\text{CH}_2$	Thermal (225–250°)	$n\text{-C}_3\text{H}_7\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}_2$ (—)	275, 598 258, 598

$\text{Br}_2(\text{CH}_3)_2\text{SiH}$		Peroxide		691
		Peroxide		591
	$[(\text{CH}_3)_3\text{Si}]_3\text{NCH}_2\text{CH}=\text{CH}_2$	Peroxide	$[(\text{CH}_3)_3\text{Si}]_3\text{N}(\text{CH}_2)_3\text{Si}(\text{CH}_3)\text{Br}_2$ (—)	601
		Peroxide		601
		Peroxide	$\text{C}_6\text{H}_4\text{Si}(\text{C}_2\text{H}_5)_2\text{Br}_2$ (44)	288
$\text{Cl}(\text{C}_2\text{H}_5)_2\text{SiH}$	$\text{CH}_2\text{CH}=\text{CH}_2$	Thermal (225–250°)	$n\text{-C}_6\text{H}_{13}\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}$ (—)	258, 598
	$\text{CH}_2\text{O}_2\text{C}(\text{CH}_3)_2\text{CH}=\text{CH}_2$	UV	$\text{CH}_2\text{O}_2\text{C}(\text{CH}_3)_2\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}$ (24–40)	598, 604
	$\text{CH}_2\text{CH}=\text{CH}_2$	Thermal (225–250°)	$n\text{-C}_6\text{H}_{13}\text{Si}(\text{CH}_3)_2\text{Cl}$ (—)	258
	$\text{CH}_2\text{CH}=\text{CH}_2$	Thermal (225–250°)	$n\text{-C}_6\text{H}_{13}\text{Si}(\text{C}_2\text{H}_5)_2\text{Cl}$ (—)	258
	$\text{CF}_3\text{CF}=\text{CF}_2$	Thermal (250°)	$(\text{CH}_3)_2\text{SiCF}_2\text{CH}_2\text{CF}_3$ (—)	279
	$\text{CF}_3\text{CF}=\text{CF}_2$	UV	$(\text{CH}_3)_2\text{SiCF}_2\text{CH}_2\text{CF}_3$ (90)	287
	$\text{CF}_3\text{CF}=\text{CF}_2$	UV	$n\text{-C}_6\text{H}_{13}\text{Si}(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2\text{CH}_3$ (79)	269
	$\text{CH}_2=\text{CH}_2$	$\text{Fe}(\text{CO})_5$	$(\text{C}_2\text{H}_5)_3\text{Si}$ (81)	284
		Thermal (300°)	$(\text{C}_2\text{H}_5)_3\text{Si}$ (15)	603, 273, 275
			$(\text{C}_2\text{H}_5)_3\text{SiC}_2\text{H}_5$ (6)	
			and higher telomers	
	$\text{C}_6\text{H}_5\text{OCH}=\text{CH}_2$	$\text{Fe}(\text{CO})_5$	$(\text{C}_6\text{H}_5)_3\text{SiCH}=\text{CHOC}_2\text{H}_5$ (—)	264
	$\text{CH}_2=\text{CH}_2$	$\text{Fe}(\text{CO})_5$	$(\text{C}_6\text{H}_5)_3\text{SiCH}=\text{CHOC}_2\text{H}_5$ (65)	264
	$\text{CH}_2=\text{CH}_2$	Thermal (330°)	$(n\text{-C}_6\text{H}_{13})_2\text{Si}(\text{CH}_2\text{CH}_3)_2\text{H}$ (—)	582
			[a = 3, 4, 5]	

Note: References 385 to 631 are on pp. 371–376.

TABLE XI—Continued
C. Silanes and Other Substituted Silanes and Olefins—Continued

Silane	Olefin	Catalyst	Product (%)	Refs.
$(C_6H_5)_3SiH$				
	$(CH_3)_3SiCH_2CH=CH_2$	Peroxide	$(CH_3)_3Si(CH_2)_3Si(C_6H_5)_3$ (3)	293
	$n-C_4H_9CH=CH_2$	Peroxide	$n-C_4H_9Si(C_6H_5)_3$ (54)	265
	$n-C_6H_{13}CH=CH_2$	Peroxide	$n-C_{10}H_{21}Si(C_6H_5)_3$ (25)	603
	$HO_2C(CH_2)_8CH=CH_2$	Peroxide	$HO_2C(CH_2)_8Si(C_6H_5)_3$ (96)	606
	$n-C_4H_9CH=CH_2$	Peroxide	$n-C_{12}H_{25}Si(C_6H_5)_3$ (46)	291
	$n-C_{10}H_{21}CH=CH_2$	Peroxide	$C_2H_5O_2C(CH_2)_{10}Si(C_6H_5)_3$	606
	$C_2H_5O_2C(CH_2)_8CH=CH_2$	Peroxide	$n-C_{14}H_{29}Si(C_6H_5)_3$ (52)	291
	$n-C_4H_9CH=CH_2$	Peroxide	$n-C_{12}H_{25}Si(C_6H_5)_3$ (45)	291
	$n-C_{10}H_{21}CH=CH_2$	Peroxide	$n-C_{14}H_{29}Si(C_6H_5)_3$ (40)	291
	$(C_6H_5)_3SiCH_2CH=CH_2$	Peroxide	$(C_6H_5)_3Si(CH_2)_3Si(C_6H_5)_3$ (36)	293, 312


D. Silanes and Acetylenes

Silane	Acetylene	Catalyst	Product (%)	Refs.
Cl_3SiH				
	$HCl=CH$	Peroxide	$Cl_3Si(CH_2)_3SiCl_3$ (3)	257, 607
		Hot tube	$Cl_3SiCH=CH_2$ (—)	295
	$n-C_3H_7C\equiv CH$	Peroxide	$n-C_3H_7CH=CHSiCl_3$ (38)	283, 285
		Peroxide	$n-C_3H_7CH=CHSiCl_3$ (20)	282
		Thermal	$n-C_3H_7CH=CHSiCl_3$ (—)	582
		UV	$n-C_3H_7CH=CHSiCl_3$ (—)	582
	$i-C_3H_7C\equiv CH$	Peroxide	$i-C_3H_7CH=CHSiCl_3$ (37)	285
	$n-C_4H_9C\equiv CH$	Thermal	$n-C_4H_9CH=CHSiCl_3$ (15)	608
		Peroxide	$n-C_4H_9CH=CHSiCl_3$ (36)	283, 285
	$i-C_4H_9C\equiv CH$	Peroxide	$i-C_4H_9CH=CHSiCl_3$ (39)	285
	$(CH_3)_3SiC\equiv CCH_3$	Peroxide	$(CH_3)_3SiC(SiCl_3)=CHCH_3$ (—)	284
	$n-C_2H_5C\equiv CH$	Peroxide	$n-C_2H_5CH=CHSiCl_3$ (47)	283, 285

Note: References 385 to 631 are on pp. 371–376.

TABLE XII

ADDITION OF GERMANES TO UNSATURATES

Germane	Unsaturate	Catalyst	Product (%)	Refs.
Cl_3GeH	$\text{HC}=\text{CH}$	None added	$\text{Cl}_3\text{GeCH}_2\text{CH}_2\text{GeCl}_3$ (90)	315
	$\text{CH}_2=\text{CH}_2$	None added	$\text{CH}_3\text{CH}_2\text{GeCl}_3$ (58)	315
	$\text{CH}_2=\text{CHCl}$	None added	$\text{CH}_3\text{CH}_2\text{GeCl}_3$ (33)	315
	$\text{CHCl}=\text{CHSnCl}_3$	None added	$\text{Cl}_3\text{SnCH}_2\text{CHClGeCl}_3$ (52)	315
	$\text{CH}_2=\text{CHSnCl}_3$	None added	$\text{Cl}_3\text{SnCH}_2\text{CH}_2\text{GeCl}_3$ (83)	315
	$\text{CH}_2=\text{CHCN}$	None added	$\text{NCCH}_2\text{CH}_2\text{GeCl}_3$ (53)	315
	$\text{CH}_2=\text{CHCH}_2\text{Cl}$	None added	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{GeCl}_3$ (77)	315
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{Cl}$	None added	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{GeCl}_3$ (58)	315
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$\text{C}_4\text{H}_9\text{GeCl}_3$ (21)	609
	$\text{CH}_2=\text{CHCH}_2\text{OOCCH}_3$	None added	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{GeCl}_3$ (41)	315
	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Peroxide	$\text{C}_6\text{H}_{13}\text{GeCl}_3$ (10)	609
	Difluorohexane	Peroxide	$\text{C}_6\text{H}_{11}\text{FGeCl}_3$ (22)	609
	Chlorohexane	Peroxide	$\text{C}_6\text{H}_{11}\text{ClGeCl}_3$ (16)	609
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$\text{C}_4\text{H}_9\text{GeCl}_3$ (24)	609
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$\text{C}_4\text{H}_9\text{GeCl}_3$ (18)	609
	Methylstyrene	Peroxide	$\text{C}_8\text{H}_{11}\text{GeCl}_3$ (10)	609
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$\text{C}_4\text{H}_9\text{GeCl}_3$ (11-22)	610, 609
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$\text{C}_4\text{H}_9\text{GeCl}_3$ (53)	315
	$\text{CH}_2=\text{CHCN}$	Peroxide	$\text{C}_4\text{H}_9\text{GeCl}_3$ (9)	609
	$\text{CH}_2=\text{CHCO}_2\text{H}$	None added	$(\text{C}_2\text{H}_5)_2\text{GeCH}_2\text{CH}_2\text{CN}$ (—)	310
	$\text{CH}_2=\text{CHCO}_2\text{H}$	None added	$(\text{C}_2\text{H}_5)_2\text{GeCH}_2\text{CH}_2\text{CO}_2\text{H}$ (—)	310
	$\text{CH}_2=\text{CHCH}_2\text{OH}$	Peroxide	$(n\text{-C}_4\text{H}_9)_2\text{GeCH}_2\text{CH}_2\text{CH}_2\text{OH}$ (—)	310
	$\text{CH}_2=\text{CHCN}$	None added	$(n\text{-C}_4\text{H}_9)_2\text{GeCH}_2\text{CH}_2\text{CN}$ (—)	310
	$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(n\text{-C}_4\text{H}_9)_2\text{GeCH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ (—)	310
	$\text{CH}_2=\text{CHCH}_2\text{OH}$	Peroxide	$(n\text{-C}_4\text{H}_9)_2\text{GeCH}_2\text{CH}_2\text{CH}_2\text{OH}$ (—)	310
	$\text{CH}_2=\text{CHCN}$	None added	$(n\text{-C}_4\text{H}_9)_2\text{GeCH}_2\text{CH}_2\text{CN}$ (—)	310
		Peroxide or UV	1:1 adduct and $(\text{C}_4\text{H}_9)_3\text{Ge}$ (—)	314
				
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_4\text{H}_9\text{Ge}(\text{C}_2\text{H}_5)_3$ (91)	314
	$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	UV	$n\text{-C}_4\text{H}_9\text{Ge}(\text{C}_2\text{H}_5)_3$ (80)	314
	$\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_5$	Peroxide	$n\text{-C}_4\text{H}_9\text{Ge}(\text{C}_2\text{H}_5)_3$ (67)	311
	$\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_5$	Peroxide	$(\text{C}_2\text{H}_5)_3\text{Ge}(\text{CH}_2)_3\text{Ge}(\text{C}_2\text{H}_5)_3$ (87)	311
	$\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_5$	Peroxide	$(\text{C}_2\text{H}_5)_3\text{Ge}(\text{CH}_2)_3\text{Sn}(\text{C}_2\text{H}_5)_3$ (76)	312

Note: References 385 to 431 are on pp. 371-376



TABLE XI—Continued
C. Silane and Other Substituted Silanes and Olefins—Continued

Silane	Olefin	Catalyst	Product (%)	Refs.
(C ₂ H ₅) ₃ SiH	(CH ₃) ₃ SiCH ₂ CH=CH ₂	Peroxide	(CH ₃) ₃ Si(CH ₂) ₃ Si(C ₂ H ₅) ₃ (3)	293
	n-C ₄ H ₉ CH=CH ₂	Peroxide	n-C ₄ H ₉ Si(C ₂ H ₅) ₃ (54)	265
	n-C ₄ H ₉ CH=CH ₂	Peroxide	n-C ₄ H ₉ Si(C ₂ H ₅) ₃ (25)	603
	HO ₂ C(CH ₂) ₂ CH=CH ₂	Peroxide	HO ₂ C(CH ₂) ₂ Si(C ₂ H ₅) ₃ (90)	606
	n-C ₁₀ H ₁₉ CH=CH ₂	Peroxide	n-C ₁₀ H ₁₉ Si(C ₂ H ₅) ₃ (46)	291
	C ₂ H ₅ O ₂ C(CH ₂) ₂ CH=CH ₂	Peroxide	C ₂ H ₅ O ₂ C(CH ₂) ₂ Si(C ₂ H ₅) ₃	606
	n-C ₁₁ H ₂₃ CH=CH ₂	Peroxide	n-C ₁₁ H ₂₃ Si(C ₂ H ₅) ₃ (52)	291
	n-C ₁₁ H ₂₃ CH=CH ₂	Peroxide	n-C ₁₁ H ₂₃ Si(C ₂ H ₅) ₃ (45)	291
	n-C ₁₁ H ₂₃ CH=CH ₂	Peroxide	n-C ₁₁ H ₂₃ Si(C ₂ H ₅) ₃ (40)	291
	(C ₆ H ₅) ₃ SiCH ₂ CH=CH ₂	Peroxide	(C ₆ H ₅) ₃ Si(CH ₂) ₃ Si(C ₂ H ₅) ₃ (36)	293, 312

D. Silanes and Acetylenes

Silane	Acetylene	Catalyst	Product (%)	Refs.
Cl ₃ SiH	HC≡CH	Peroxide	Cl ₃ Si(CH ₂) ₃ SiCl ₃ (3)	257, 607
		Hot tube	Cl ₃ SiCH=CH ₂ (—)	295
	n-C ₃ H ₇ C≡CH	Peroxide	n-C ₃ H ₇ CH=CHSiCl ₃ (38)	283, 285
		Peroxide	n-C ₃ H ₇ CH=CHSiCl ₃ (20)	282
		Thermal	n-C ₃ H ₇ CH=CHSiCl ₃ (—)	582
		UV	n-C ₃ H ₇ CH=CHSiCl ₃ (—)	582
		Peroxide	i-C ₃ H ₇ CH=CHSiCl ₃ (37)	285
		Thermal	n-C ₃ H ₇ CH=CHSiCl ₃ (15)	608
		Peroxide	n-C ₃ H ₇ CH=CHSiCl ₃ (36)	283, 285
		Peroxide	i-C ₃ H ₇ CH=CHSiCl ₃ (39)	285
		Peroxide	(CH ₃) ₃ SiC(SiCl ₃)=CHCH ₃ (—)	284
		Peroxide	n-C ₃ H ₇ CH=CHSiCl ₃ (47)	283, 285

Note: References 385 to 631 are on pp. 371–376.


$\text{CH}_3\text{OCH}=\text{CH}_2$	UV	$\text{CH}_3\text{OCH}_2\text{CH}_2\text{PH}_2$ (—)	310, 615
$\text{CH}_3=\text{CHCH}_2\text{OH}$	UV	$(\text{CH}_3\text{OCH}_2\text{CH}_2)_3\text{PH}$ (—)	
$\text{CH}_3=\text{CHCH}_2\text{NH}_2$	UV	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{PH}_2$ (26)	316, 317, 615
$(\text{CH}_3)_2\text{C}=\text{CF}_2$	None added	$(\text{HOCH}_2\text{CH}_2\text{CH}_2)_3\text{P}$ (3)	
$\text{CH}_3\text{O}_2\text{CCH}=\text{CH}_2$	UV	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{PH}_2$ (28)	316, 317, 615
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	UV or peroxide	$(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2)_3\text{P}$ (—)	
$\text{CH}_3\text{CR}=\text{CHCH}_3$	Peroxide	$(\text{CH}_3)_3\text{CHCF}_2\text{PH}_2$ (6)	331
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	Azonitrile or UV + acetone	$\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}_2\text{PH}_2$ (—)	316, 615
$\text{C}_6\text{H}_5\text{O}_2\text{CCH}=\text{CH}_2$	Azonitrile	$(\text{CH}_3)_3\text{CHCH}_2\text{CH}_2\text{PH}_2$ (10)	316, 317, 615
		$(\text{C}_6\text{H}_5)_3\text{P}$ (2)	318, 615
		$\text{CH}_3\text{CH}(\text{C}_6\text{H}_5)_2\text{PH}_2$ (—)	315, 615, 316
		$(\text{CH}_3)_2\text{CHCH}_2\text{PH}_2$ (13-34)	
		$(\text{CH}_3)_3\text{CHCH}_2\text{CH}_2\text{PH}_2$ (24-52)	
		$(\text{CH}_3)_3\text{CHCH}_2\text{CH}_2\text{P}$ (7-21)	318
		$\text{C}_6\text{H}_5\text{O}_2\text{CCH}_2\text{CH}_2\text{PH}_2$ (21)	
		$(\text{C}_6\text{H}_5)_2\text{CCH}_2\text{CH}_2\text{PH}_2$ (19-20)	
		$(\text{C}_6\text{H}_5)_2\text{CCH}_2\text{CH}_2\text{P}$ (24)	
		$(\text{C}_6\text{H}_5)_3\text{CCH}_2\text{CH}_2\text{PCH}_3$	
		$\text{CH}(\text{CO}_2\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_6\text{H}_5$ (9-19)	
	Azonitrile or UV	 PH_2 (43)	315, 316
	Azonitrile	 PH (29)	317, 615
$n\text{-C}_6\text{H}_{13}\text{OCH}=\text{CH}_2$	Azonitrile	$n\text{-C}_6\text{H}_{13}\text{OCH}_2\text{CH}_2\text{PH}_2$ (45)	318
$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	Azonitrile	$(n\text{-C}_6\text{H}_{13}\text{OCH}_2\text{CH}_2)_3\text{PH}$ (30)	
		$(n\text{-C}_6\text{H}_{13}\text{OCH}_2\text{CH}_2)_3\text{P}$ (10)	
		$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{PH}_2$ (36)	318
		$(\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2)_3\text{PH}$ (29)	
		$(\text{C}_6\text{H}_5)_3\text{CH}_2\text{CH}_2\text{P}$ (6)	

Note: References 385 to 631 are on pp 371-376.

TABLE XIII

FORMATION OF PHOSPHORUS-CARBON BONDS



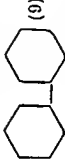
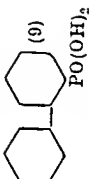
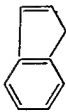
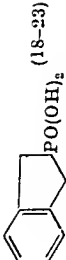
A. *Phosphorus Trichloride*




Phosphorus Compound	Unsaturate	Catalyst	Product (%)	Refs.
PCl ₃	CH ₂ =CHC ₂ H ₅ + O ₂		C ₂ H ₅ CHClCH ₂ POCl ₂ C ₂ H ₅ CH(CH ₂ Cl)POCl ₂ } (7.5)	341
	CH ₃ CH=CHCH ₃ + O ₂		CH ₃ CHClCH(CH ₃)POCl ₂ (20) CH ₃ CHClCH(CH ₃)POCl ₂ (31)	341
	 + O ₂		C ₆ H ₁₀ ClPOCl ₂ } (40) C ₆ H ₉ POCl ₂	341
	 CH=CH ₂	UV	 CHClCH ₂ POCl ₂ (17)	611
	CH ₂ =CHC ₆ H ₁₃ ⁿ	Peroxide	n-C ₆ H ₁₃ CHClCH ₂ POCl ₂ (33)	340, 612-614

B. *Phosphines*

Phosphorus Compound	Unsaturate	Catalyst	Product (%)	Refs.
PH ₃	CFCl=CF ₂	None added	CHFClCF ₂ PH ₂ (54) (CHFClCF ₂) ₂ PH (6) H ₂ POFCICF ₂ PH ₂ (1) CHCl ₂ CF ₂ PH ₂ (30) (CHCl ₂ CF ₂) ₂ PH (3) H ₂ POCl ₂ CF ₂ PH ₂ (—)	331
	CCl ₂ =CF ₂	None added	CHF ₂ CF ₂ PH ₂ (53) (CHF ₂ CF ₂) ₂ PH (7) H ₂ POCF ₂ CF ₂ PH ₂ (8) ClHF ₂ CH ₂ PH ₂ (1)	331
	CF ₃ =CF ₂	None added	CF ₃ CF(PH ₂)CF ₂ H (36) CH ₃ ClCH ₂ CH ₂ PH ₂ (—) (CH ₂ ClCH ₂ CH ₂) ₂ PH (—) (CH ₃ ClCH ₂ CH ₂) ₂ P + phosphorus-containing polymer	331 331 316, 317, 615
	CF ₂ =CH ₂	None added		
	CF ₃ CF=CF ₂	None added		
	Cl ₂ ClCH=CH ₂	UV		

TABLE XIII—Continued

C. Hypophosphorous Acid and Salts—Continued			
Phosphorus Compound $\text{H}_2\text{P}(\text{O})\text{ONa}$	Unsaturate	Catalyst	Product (%)
	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{OH}$	Peroxide	$\text{HOCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{PH}(\text{O})\text{ONa}$ (—)
	$\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{OH}$	Peroxide	$\text{HO}(\text{CH}_2)_3\text{PH}(\text{O})\text{ONa}$ (—)
	$\text{CH}_2=\text{CHC}_6\text{H}_9^{\text{n}}$	Peroxide	$n\text{-C}_8\text{H}_{17}\text{PH}(\text{O})\text{ONa}$ (100)
	$\text{CH}_2=\text{CHC}_6\text{H}_{13}^{\text{n}}$	Peroxide	$n\text{-C}_8\text{H}_{17}\text{PH}(\text{O})\text{ONa}$ (100)
	$\text{CH}_2=\text{CHC}_6\text{H}_{15}^{\text{n}}$	Peroxide	$n\text{-C}_{14}\text{H}_{29}\text{PH}(\text{O})\text{ONa}$ (80)
			327, 328, 618 327, 328, 618
D. Phosphorous Acid and Esters			
$\text{HPO}(\text{OH})_2$		Peroxide	 (20)
			320, 321
		Peroxide	 (9)
			320
	$\text{CH}_2=\text{CHC}_4\text{H}_9^{\text{n}}$	Peroxide	$n\text{-C}_6\text{H}_{13}\text{PO}(\text{OH})_2$ (23)
			$n\text{-C}_6\text{H}_{13}\text{CH}(\text{C}_4\text{H}_9^{\text{n}})\text{CH}_2\text{PO}(\text{OH})_2$ (8)
	$\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$	None added	$(\text{HO})_2\text{P}(\text{O})\text{CHCO}_2\text{C}_2\text{H}_5$ (16)
			$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$
	$\text{CH}_2=\text{CHC}_6\text{H}_{13}^{\text{n}}$	Peroxide or UV	$n\text{-C}_8\text{H}_{17}\text{PO}(\text{OH})_2$ (18-28)
			$n\text{-C}_8\text{H}_{17}\text{CH}(\text{C}_6\text{H}_{13}^{\text{n}})\text{CH}_2\text{PO}(\text{OH})_2$ (—) + high mol. wt. oil
		Peroxide or UV	 (18-23) + high mol.-wt. oil
			321



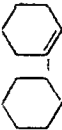

	$\text{CH}_2\text{CH}_2\text{S}(\text{CH}_2)_n(\text{OC}_2\text{H}_5)_2$	Peroxide	$(\text{C}_2\text{H}_5\text{O})_2\text{S}(\text{CH}_2)_n\text{CH}_2\text{CH}_2$  - $\text{PO}(\text{OC}_2\text{H}_5)_2$ (52)	322
$\text{C}_6\text{H}_5\text{OCH}_2\text{CH}=\text{CH}_2$		Peroxide	$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_n\text{PO}(\text{OC}_2\text{H}_5)_2$ (55)	622, 627
$n \text{ C}_6\text{H}_5\text{CO}_2\text{CH}=\text{CH}_2$		Peroxide	$n \text{ C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (57)	334
$n \text{ C}_6\text{H}_5(\text{C}_6\text{H}_4)_n\text{CH}=\text{CH}_2$		Peroxide	$n \text{ C}_6\text{H}_5(\text{C}_6\text{H}_4)_n\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (—)	330
$\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$		Peroxide or UV	$(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{OCH}_2\text{CH}_2)_n\text{CO}_2$ $\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)_2\text{C}_6\text{H}_4$ (53)	334
$n \text{ C}_6\text{H}_5\text{CO}_2\text{CH}=\text{CH}_2$		Peroxide	$n \text{ C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (49)	334
$\text{CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$		Peroxide	$\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (CH_2) ₁₀ $\text{CO}_2\text{C}_6\text{H}_5$ (75)	334
$n \text{ C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_4)_n\text{CH}=\text{CH}_2$		Peroxide	$n \text{ C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_4)_n\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (—)	320
$\text{CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$		Peroxide	$\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (CH_2) ₁₀ $\text{CO}_2\text{C}_6\text{H}_5$ (57)	334
$\text{CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{CH}_2\text{CH}=\text{CH}_2$		Peroxide	$\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{OCO}$ $n \text{ C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_4)_n\text{CH}_2\text{CH}_2\text{OCO}$	334
$\text{HOCH}_2\text{CH}=\text{CH}_2$		Peroxide	$\text{HO}(\text{CH}_2)_n\text{PO}(\text{OC}_2\text{H}_5)_2$ (50)	327, 328
$n \text{ C}_6\text{H}_5\text{CH}=\text{CH}_2$		UV or peroxide	$n \text{ C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (59)	337
$\text{HOCH}_2\text{CH}=\text{CH}_2$		Peroxide	$\text{HO}(\text{CH}_2)_n\text{PO}(\text{OC}_2\text{H}_5)_2$ (30)	327, 328
$\text{CH}_2\text{CH}=\text{CHCH}_2$		Peroxide	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_2)_n\text{PO}(\text{OC}_2\text{H}_5)_2$ (77)	334
$\text{C}_6\text{H}_5\text{CO}_2\text{CH}=\text{CH}_2$		Peroxide	$\text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (45)	334
$(\text{CH}_2)_n\text{SiCH}=\text{CH}_2$		Peroxide	$(\text{CH}_2)_n\text{SiCH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (53)	322
		Peroxide	$\text{PO}(\text{OC}_2\text{H}_5)_2$ (52)	327, 328, 334
$(\text{CH}_2)_n\text{CHCH}_2\text{O}$		Peroxide	$[\text{C}_6\text{H}_5\text{O}]_n\text{PO}(\text{CH}_2)_n\text{O}$ $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (58)	327, 328
$n \text{ C}_6\text{H}_5\text{CO}_2\text{CH}=\text{CH}_2$		Peroxide	$n \text{ C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (58)	334
$\text{CH}_2\text{CH}=\text{CHCO}_2\text{C}_6\text{H}_5$		Peroxide	$[\text{C}_6\text{H}_5\text{O}]_n\text{POCH}(\text{CH}_2)_n\text{CO}_2\text{C}_6\text{H}_5$ (30)	327, 328
$n \text{ C}_6\text{H}_5\text{CH}=\text{CH}_2$		UV or peroxide	$n \text{ C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$ (55) + higher telomers (19)	327, 618, 337, 328, 324







Note. References 385 to 631 are on pp. 371-376.

$\text{HPO}(\text{OC}_2\text{H}_5)_2$
 $\text{HPO}(\text{OC}_2\text{H}_5)_n$

TABLE XIII—Continued

D. Phosphorous Acid and Esters—Continued

Phosphorous Compound HPO(OC ₂ H ₅) ₂ (cont.)	Unsaturated	Catalyst	Product (%)	Refs.
	CH ₃ CO ₂ C(CH ₃)=CH ₂	Peroxide	CH ₃ CO ₂ CH(CH ₃)CH ₂ PO(OC ₂ H ₅) ₂ (72) + higher telomers (16)	333
	C ₂ H ₅ CO ₂ CH=CH ₂	Peroxide	C ₂ H ₅ CO ₂ CH ₂ CH ₂ PO(OC ₂ H ₅) ₂ (55)	334
		UV	 PO(OC ₂ H ₅) ₂ (—) + polymer	337
	n-C ₈ H ₁₇ CO ₂ CH=CH ₂	Peroxide UV or peroxide	n-C ₈ H ₁₇ CO ₂ CH ₂ CH ₂ PO(OC ₂ H ₅) ₂ (45)	334
	n-C ₈ H ₁₇ CH=CH ₂	UV	n-C ₈ H ₁₇ PO(OC ₂ H ₅) ₂ (29)	327, 328, 32 I, 337
	n-C ₁₁ H ₂₃ CH=CHCH ₃	UV	n-C ₁₁ H ₂₃ CH(CH ₃)PO(OC ₂ H ₅) ₂ (18)	337
	C ₂ H ₅ OSi(CH ₃) ₂ CH=CH ₂	Peroxide UV	C ₂ H ₅ OSi(CH ₃) ₂ CH ₂ CH ₂ PO(OC ₂ H ₅) ₂ (55)	322
	n-C ₈ H ₁₇ CH=CHCH ₃	UV	n-C ₈ H ₁₇ CH(CH ₃)PO(OC ₂ H ₅) ₂ (30)	337
	C ₂ H ₅ OSi(CH ₃) ₂ CH ₂ CH=CH ₂	Peroxide	C ₂ H ₅ OSi(CH ₃) ₂ CH ₂ CH ₂ CH ₂ PO(OC ₂ H ₅) ₂ (62)	322
	(C ₂ H ₅) ₃ Si(CH ₃)CH=CH ₂	Azonitrile or peroxide	(C ₂ H ₅) ₃ Si(CH ₃)CH ₂ CH ₂ PO(OC ₂ H ₅) ₂ (37-48)	619, 322, 620
	n-C ₈ H ₁₇ CH=CH ₂	Peroxide, azo- nitrile, or UV	n-C ₈ H ₁₇ PO(OC ₂ H ₅) ₂ (13-60)	323, 337, 621
	(C ₂ H ₅) ₂ SiCH=CH ₂	Peroxide	(C ₂ H ₅) ₂ SiCH ₂ CH ₂ PO(OC ₂ H ₅) ₂ (33)	322
	n-C ₇ H ₁₅ CH=CH ₂	UV or peroxide	n-C ₇ H ₁₅ PO(OC ₂ H ₅) ₂ (50)	337
	n-C ₈ H ₁₇ CH=CH ₂	UV or peroxide	n-C ₈ H ₁₇ PO(OC ₂ H ₅) ₂ (37)	337
	n-C ₈ H ₁₇ CO ₂ CH=CH ₂	Peroxide	n-C ₈ H ₁₇ CO ₂ CH ₂ CH ₂ PO(OC ₂ H ₅) ₂ (50)	334
		Peroxide	(—)  PO(OC ₂ H ₅) ₂	320
	n-C ₁₀ H ₁₉ CH=CH ₂	Peroxide	n-C ₁₀ H ₁₉ PO(OC ₂ H ₅) ₂ (86)	621
	n-C ₆ H ₁₃ CH(CH ₃)CH=CH ₂	Peroxide	n-C ₆ H ₁₃ CH(CH ₃)CH ₂ PO(OC ₂ H ₅) ₂ (—)	320
	CH ₂ =CH(CH(CH ₃) ₂)CO ₂ C ₂ H ₅	Peroxide or UV	(C ₂ H ₅) ₂ P(O)(CH ₂) ₆ CO ₂ C ₂ H ₅ (58)	334

Phosphorus Compound	Unsaturated	Esters of Thiophosphorous Acid	Catalyst	Product (%)	Refs
HPs(OC ₂ H ₅) ₂	n C ₁₇ H ₃₅ CO ₂ CH=CH ₂	Peroxide	UV or peroxide	n C ₁₇ H ₃₅ CO ₂ CH ₂ CH ₂ PO IOCH ₂ CH(C ₂ H ₅)C ₂ H ₅ n) (46)	334
	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇	Peroxide	UV or peroxide	CH ₃ (CH ₂) ₇ CH- [PO(OCH ₂) ₂ CH(C ₂ H ₅)C ₂ H ₅ n)] ₂ (CH ₂) ₁₄	334
	n C ₁₇ H ₃₅ CH(C ₂ H ₅)CH ₂ OCO			n C ₁₇ H ₃₅ CH(C ₂ H ₅)CH ₂ OCO (87)	
HPs(OC ₂ H ₅) ₂		UV or peroxide	UV or peroxide	 PS(OC ₂ H ₅) ₂ (61)	339
	n C ₂ H ₅ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₂ H ₅ PS(OC ₂ H ₅) ₂ (60)	339
	n C ₄ H ₉ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₄ H ₉ PS(OC ₂ H ₅) ₂ (60)	339
	n C ₈ H ₁₇ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₈ H ₁₇ PS(OC ₂ H ₅) ₂ (30)	339
	n C ₁₇ H ₃₅ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₁₇ H ₃₅ PS(OC ₂ H ₅) ₂ (54)	339
HPs(OC ₂ H ₅) ₂		UV or peroxide	UV or peroxide	 PS(OC ₂ H ₅) ₂ (44)	339
	n C ₂ H ₅ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₂ H ₅ PS(OC ₂ H ₅) ₂ (43)	339
	n C ₄ H ₉ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₄ H ₉ PS(OC ₂ H ₅) ₂ (38)	339
	n C ₈ H ₁₇ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₈ H ₁₇ PS(OC ₂ H ₅) ₂ (40)	339
	n C ₁₇ H ₃₅ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₁₇ H ₃₅ PS(OC ₂ H ₅) ₂ (41)	339
HPs(OC ₂ H ₅) ₂		UV or peroxide	UV or peroxide	 PS(OC ₂ H ₅) ₂ (58)	339
	n C ₂ H ₅ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₂ H ₅ PS(OC ₂ H ₅) ₂ (33)	339
	n C ₄ H ₉ CH=CH ₂	UV or peroxide	UV or peroxide	n C ₄ H ₉ PS(OC ₂ H ₅) ₂ (66)	339

Note. References 333 to 431 are on pp. 371-376.

TABLE XIII—Continued
D. Phosphorous Acid and Esters—Continued

Phosphorus Compound	Unsaturate	Catalyst	Product (%)	Refs.
$\text{HPO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (contd.)				
	$(\text{CH}_3)_2\text{CCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	Peroxide	$(\text{CH}_3)_2\text{CCH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (42)	324
	$n\text{-C}_4\text{H}_9\text{OSi}(\text{CH}_3)_2\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_4\text{H}_9\text{OSi}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (59)	322
	$(\text{C}_2\text{H}_5\text{O})_2\text{SiCH}=\text{CH}_2$	Azonirile	$(\text{C}_2\text{H}_5\text{O})_2\text{SiCH}_2\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (37)	619, 620
	$n\text{-C}_8\text{H}_{17}\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_{10}\text{H}_{21}\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (25)	328, 327, 324
	$n\text{-C}_8\text{H}_{17}\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_{10}\text{H}_{21}\text{CH}(\text{C}_4\text{H}_9\text{-}n)\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (25)	334
	$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CO}_2\text{C}_4\text{H}_9\text{-}n$	UV or peroxide	$n\text{-C}_8\text{H}_{17}\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (45)	334
	$n\text{-C}_{12}\text{H}_{27}\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide	$(n\text{-C}_8\text{H}_{17}\text{O})_2\text{P}(\text{O})(\text{CH}_2)_{10}\text{CO}_2\text{C}_4\text{H}_9\text{-}n$ (66)	334
	$n\text{-C}_{17}\text{H}_{33}\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_8\text{H}_{17}\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (60)	334
	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_2\text{H}_5$	Peroxide	$n\text{-C}_{17}\text{H}_{33}\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2$ (47)	334
			$\text{CH}_3(\text{CH}_2)_{10}\text{CH}(\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2)(\text{CH}_2)_{17}\text{CO}_2\text{C}_2\text{H}_5$ (77)	334
	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_4\text{H}_9\text{-}n$	Peroxide	$\text{CH}_3(\text{CH}_2)_{10}\text{CH}(\text{PO}(\text{OC}_4\text{H}_9\text{-}n)_2)(\text{CH}_2)_{17}\text{CO}_2\text{C}_4\text{H}_9\text{-}n$	334
			$n\text{-C}_4\text{H}_9\text{OCO}$	
	$\text{C}_2\text{H}_5\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide	$\text{C}_2\text{H}_5\text{CO}_2(\text{CH}_2)_2\text{PO}(\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{-C}_4\text{H}_9\text{-}n)_2$ (45)	334
	$n\text{-C}_3\text{H}_7\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide	$n\text{-C}_4\text{H}_9\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}$	334
	$n\text{-C}_8\text{H}_{17}\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide	$[\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9\text{-}n]_2$ (52)	334
	$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CO}_2\text{C}_2\text{H}_5$	UV or peroxide	$[\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9\text{-}n]_2$ (49)	334
	$n\text{-C}_{13}\text{H}_{27}\text{CO}_2\text{CH}=\text{CH}_2$	Peroxide	$\text{P}(\text{O})(\text{CH}_2)_{10}\text{CO}_2\text{C}_2\text{H}_5$ (53)	334
			$n\text{-C}_{13}\text{H}_{27}\text{CO}_2\text{CH}_2\text{CH}_2\text{PO}$	334
			$[\text{OCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9\text{-}n]_2$ (49)	
	$\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CO}_2\text{CH}_2\text{-CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9\text{-}n$	UV or peroxide	$[\text{-C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{O}]_2\text{P}(\text{O})(\text{CH}_2)_{10}$ (61)	334
			$n\text{-C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OCO}$	

TABLE XIV

FORMATION OF CARBON-NITROGEN BONDS

(This table includes only reactions reported since 1945 See p 225)







A. Addition of Diminogen Tetrazide to Olefins and Acetylenes

Olefin	Conditions	Product (%)	Refs.
$CF_2=CCl_2$	65°/6 hr.	$O_2NCF_2CCl_2NO_2$ (47)	365
$CF_2=CFCl$	65°/6 hr.	$O_2NCF_2CFClNO_2$ (51)	365
$CF_2=CF_2$	65°/6 hr.	$O_2NCF_2CF_2NO_2$ (53)	365, 364
$CH_2=CH_2$	CCl_4 /press /40-60°	$O_2NCH_2CH_2NO_2$	623
		$O_2NCH_2CH_2OH^*$	
		$O_2NCH_2CH_2NO_2$ (35-40)	362
		$O_2NCH_2CH_2OH^*$ (12-20)	
		$O_2NCH_2CH_2ONO_2$ (12-20)	
		Explosive reaction on removal of solvent	
$CH_2C\equiv CH$	Ether/8 hr./0°	$CH_2CH(NO_2)CH_2NO_2$ (20-30)	368
$CH_2CH=CH_2$		$CH_2CHOHCH_2NO_2^*$ (35-40)	352
		$CH_2CH(ONO_2)CH_2NO_2$ (2-20)	
		Violent reaction	
$HC\equiv CCO\equiv CH$		$CH_2(NO_2)C\equiv C(NO_2)CH_3$ (35)	368
$CH_2C\equiv CCH_3$	Ether	$CH_2(NO_2)C\equiv C(NO_2)CH_3$ <i>trans</i> (34)	369
		$CH_2(NO_2)C\equiv C(NO_2)CH_3$ <i>cis</i> (7)	
$CH_2=CHCH=CH_2$		$O_2NCH_2CH=CHCH_2NO_2$ (14)	624
$CH_2=CHCO_2CH_3$		$O_2NCH_2CH(OHCO_2CH_3)^*$ (27)	356
		$O_2NCH=CHCO_2CH_3$ (13)†	
		$(CO_2H)_2 \cdot 2H_2O$ (80)†	
$CH_2CH=CHCO_2H$	Ether	$CH_2CHOHCH(NO_2)CO_2H$ (51)*	625








* Note References 385 to 631 are on pp 371-376

* The nitro alcohol is formed from the corresponding nitrite ester ($CONO \rightarrow COH$) by hydrolysis, in working up the reaction mixture† The unsaturated ester is presumed to come from $O_2NCH_2CH(ONO_2)CO_2CH_3$ and the oxalic acid from $O_2NCH_2CH(OHCO_2CH_3)$

TABLE XIII—Continued
F. Phosphonic Acid Derivatives

Phosphorus Compound	Unsaturate	Catalyst	Product (%)	Refs.
$C_2H_5PH(O)OCH_3$		UV or peroxide	 $P(C_2H_5)(O)OCH_3$ (40)	339
$C_2H_5PH(O)OC_2H_5$		UV or peroxide	 $P(C_2H_5)(O)OC_2H_5$ (25)	339
	$n-C_3H_7CH=CH_2$	UV or peroxide	$n-C_3H_7(C_2H_5)P(O)OC_2H_5$ (57)	339
	$n-C_3H_7CH=CH_2$	UV or peroxide	$n-C_3H_7(C_2H_5)P(O)OC_2H_5$ (65)	339
$C_2H_5PH(O)OC_4H_9 \cdot n$	$n-C_3H_7CH=CH_2$	UV or peroxide	$n-C_3H_7(C_2H_5)P(O)OC_4H_9 \cdot n$ (46)	339
$C_6H_5PH(O)OCH_3$	$n-C_3H_7CH=CH_2$	UV or peroxide	$n-C_3H_7(C_6H_5)P(O)OCH_3$ (35)	339
$C_6H_5PH(O)OC_2H_5$		UV or peroxide	 $P(C_2H_5)(O)OC_2H_5$ (33)	339
	$n-C_3H_7CH=CH_2$	UV or peroxide	$n-C_3H_7(C_2H_5)P(O)OC_2H_5$ (45)	339
	$n-C_6H_5CH=CH_2$	UV or peroxide	$n-C_6H_5(C_2H_5)P(O)OC_2H_5$ (37)	339, 328, 327
	$n-C_3H_7CH=CH_2$	UV or peroxide	$n-C_3H_7(C_6H_5)P(O)OC_2H_5$ (50)	339
$n-C_6H_5PH(O)ONa$	$n-C_3H_7CH=CH_2$	UV or peroxide	$n-C_3H_7(C_6H_5)P(O)OC_2H_5$ (71)	339
	$n-C_6H_5CH=CH_2$	Peroxide	$(n-C_6H_5)_2P(O)ONa$ (50)	327, 328


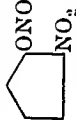

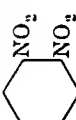
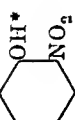
Note: References 385 to 631 are on pp. 371-376.

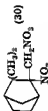
$(C_2H_5)_2C=CH_2$					
					
	Olefin to N_2O_4 in ether		352, 376		
					
					
					
	Olefin to N_2O_4 in ether		358		
		(isolated as the nitro alcohol) (<i>cis-trans</i> ratio 42:48)			
	Ether/0°	$(C_2H_5)_2C(NO_2)CH_2NO_2$ (36) $(C_2H_5)_2C(OH)CH_2NO_2^*$ (41)	627		
	Olefin to N_2O_4 in ether		358		
		(trans only) (isolated as the nitro alcohol)			

Note References 383 to 631 are on pp. 371-376

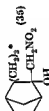
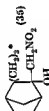
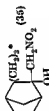
* The nitro alcohol is formed from the corresponding nitrite ester ($CONO \rightarrow COH$) by hydrolysis, in working up the reaction mixture.

TABLE XIV—Continued
A. Addition of Dinitrogen Tetroxide to Olefins and Acetylenes—Continued

Olefin	Conditions	Product (%)	Refs.
$\text{CH}_3\text{C}(\text{NO}_2)=\text{C}(\text{NO}_2)\text{CH}_3$	85°/75 hr.	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{C}(\text{NO}_2)_2\text{CH}_3$ (31)	366
$\text{C}_2\text{H}_5\text{CH}=\text{CH}_2$	Ether	$\text{C}_2\text{H}_5\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$ (39) $\text{C}_2\text{H}_5\text{CHOHCH}_2\text{NO}_2^*$ (33)	352, 353
$\text{CH}_3\text{CH}=\text{CHCH}_3$	Ether	$\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}(\text{NO}_2)\text{CH}_3$ (30) $\text{CH}_3\text{CHOHCH}(\text{NO}_2)\text{CH}_3^*$ (35)	352, 353
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	Ether	$(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{CH}_2\text{NO}_2$ (35-42) $(\text{CH}_3)_2\text{COHCH}_2\text{NO}_2^*$ (25-30) $(\text{CH}_3)_2\text{C}(\text{ONO}_2)\text{CH}_2\text{NO}_2$ (2) $\text{O}_2\text{NCH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}_2\text{NO}_2$ (5-9)	352, 353
		 (cis-trans ratio 16:84)	358
$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	-60°/no solvent	$(\text{CH}_3)_2\text{C}(\text{ONO}_2)\text{CH}(\text{NO}_2)\text{CH}_3$ (42) $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{NO}_2)\text{CH}_3^*$ (58) $\text{C}_2\text{H}_5(\text{NO}_2)\text{C}=\text{C}(\text{NO}_2)\text{C}_2\text{H}_5$ <i>trans</i> (31) <i>cis</i> (5)	626
$\text{C}_2\text{H}_5\text{C}\equiv\text{CC}_2\text{H}_5$		$\text{C}_2\text{H}_5\text{COC}(\text{NO}_2)_2\text{C}_2\text{H}_5$ (8) $\text{C}_2\text{H}_5\text{COCOC}_2\text{H}_5$ (16) $\text{C}_2\text{H}_5\text{CO}_2\text{H}$ (6) $\text{C}_2\text{H}_5\text{C}(\text{NO}_2)_2\text{C}(\text{NO}_2)_2\text{C}_2\text{H}_5$ (32) Mixture of dinitroolefins (23)	369
$\text{C}_2\text{H}_5\text{C}(\text{NO}_2)=\text{C}(\text{NO}_2)\text{C}_2\text{H}_5$ $n\text{-C}_3\text{H}_7\text{C}\equiv\text{CCCH}_3$	85°/75 hr.		366 369
	N_2O_4 to olefin in ether	 (30)  (54)	352, 376


 N_2O_4/N_2


370



370, 363

 N_2O_4/O_2


Nitro acids of unknown structure (30)

 $n-C_{11}H_{17}CH=CH_2$
 $n-C_8H_{13}CHOHCH_2NO_2^*$
 $n-C_8H_{13}CH(NO_2)CH_2NO_2^\dagger$ (mixture not separated)


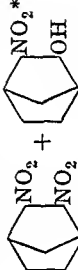
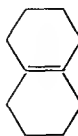
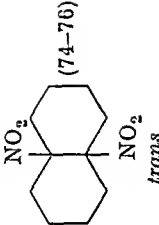
627

Note References 385 to 631 are on pp. 371-376.

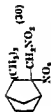
* The nitro alcohol is formed from the corresponding nitrite ester (CONO \rightarrow COH) by hydrolysis, in working up the reaction mixture

† These products were not isolated. Their identity was inferred from hydrolysis and reduction products

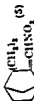
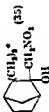
TABLE XIV—Continued
A. Addition of Dinitrogen Tetraoxide to Olefins and Acetylenes—Continued

Olefin	Conditions	Product (%)	Refs.
			361
$\text{CHCO}_2\text{C}_2\text{H}_5$ \parallel $\text{CHCO}_2\text{C}_2\text{H}_5$		<i>exo-cis</i> (16–22) <i>trans</i> (33–40) <i>trans</i> (12–14)	372
$(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	N_2O_4 to olefin in ether	$\text{ONOCHCO}_2\text{C}_2\text{H}_5 + \text{ONOCHCO}_2\text{C}_2\text{H}_5$ \mid $\text{ONOCHCO}_2\text{C}_2\text{H}_5$ $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)(\text{NO}_2)\text{CH}_2\text{NO}_2$ (30–44) $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)(\text{OH})\text{CH}_2\text{NO}_2^*$ (42–43) <i>l</i> - $\text{C}_4\text{H}_9\text{CH}=\text{C}(\text{CH}_3)_2$ (48) <i>l</i> - $\text{C}_4\text{H}_9\text{CH}(\text{NO}_2)\text{C}(\text{CH}_3)_2\text{OH}^*$ (32) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$ (34) $\text{C}_6\text{H}_5\text{CH}_2\text{CHOHCH}_2\text{NO}_2^*$ (45) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{NO}_2$ (13) $\text{C}_6\text{H}_5\text{COCH}_2\text{NO}_2$ (20) $\text{C}_6\text{H}_5\text{CH}_2\text{CHOHCH}_2\text{NO}_2^*$ (27) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_2\text{NO}_2$ (4)	352, 370 352, 376
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$	$\text{N}_2\text{O}_4/\text{N}_2$		371
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$	$\text{N}_2\text{O}_4/\text{O}_2$		371
		 <i>trans</i>	361

370



$\text{N}_2\text{O}_4/\text{N}_2$



370, 303

$\text{N}_2\text{O}_4/\text{O}_2$



Nitro acids of unknown structure (30)

$\text{C}_6\text{H}_5\text{C}(\text{OH})\text{CH}_2\text{NO}_2^*$
 $\text{C}_6\text{H}_5\text{C}(\text{HNO}_2)\text{CH}_2\text{NO}_2$

627

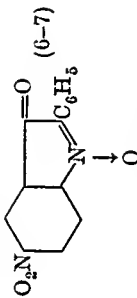
$\text{C}_6\text{H}_5\text{C}(\text{H})\text{CH}_2$

Note: Structures 263 to 431 are on pp. 371-376

* The nitro alcohol is formed from the corresponding nitro ester ($\text{ONO} \rightarrow \text{COH}$) by hydrolysis, in working up the reaction mixture.

† These products were not isolated. Their identity was inferred from hydrolysis and reduction products.

TABLE XIV—Continued
A. Addition of Dinitrogen Tetroxide to Olefins and Acetylenes—Continued

Olefin	Conditions	Product (%)	Refs.
$C_6H_5CH=CHCO_2C_2H_5$		$C_6H_5CH(ONO)CH(NO_2)CO_2C_2H_5$ or $C_6H_5CH(NO_2)CH(ONO)CO_2C_2H_5$ $C_6H_5CH(NO_2)CH(NO_2)CO_2C_2H_5$ $C_6H_5CH(NO)CH(ONO)CO_2C_2H_5$ $CH_2OHCH(NO_2)(CH_3)_8CO_2H^*$ $C_6H_5(NO_2)C=C(NO_2)C_6H_5$ <i>trans</i> (19) <i>cis</i> (25)	628
$CH_2=CH(CH_2)_8CO_2H$ $C_6H_5C\equiv CC_6H_5$	Ether/0°		373 367
		 (6-7)	
$C_6H_5CH=CHC_6H_5$	N_2O_4/N_2	+ an intractable oil $C_6H_5CH(NO_2)CH(NO_2)C_6H_5$ <i>meso</i> (21-25) \pm (32-39) $C_6H_5CH(OH)CH(NO_2)C_6H_5$ <i>erythro</i> (9-10) <i>threo</i> (13-18) $C_6H_5CH(ONO_2)CH(NO_2)C_6H_5$ (25) <i>erythro</i> (65) <i>threo</i> (35) $C_6H_5COCH(NO_2)C_6H_5$ (24) $C_6H_5CHOCH(NO_2)C_6H_5$ (29) <i>erythro</i> and <i>threo</i> $C_6H_5(NO_2)C\equiv C=C=C(NO_2)C_6H_5$ (34)	363, 362
	N_2O_4/O_2		363
$C_6H_5C\equiv CC\equiv CC_6H_5$	-25°		368



624

B. Addition of Nitryl Chloride to Olefins and Acetylenes

Olefin	Product (%)	Ref.
$\text{ClC}\equiv\text{CCl}$	$\text{Cl}(\text{NO}_2)\text{C}\equiv\text{CCl}_2$	380
$\text{CCl}_2=\text{CCl}_2$	$\text{CCl}_2\text{CCl}_2\text{NO}_2$	370
$\text{CF}_2=\text{CF}_2$	$\text{CF}_2\text{CFCF}_2\text{NO}_2$ (57)	365
$\text{CCl}_3=\text{CHCl}$	$\text{CCl}_3\text{CHClNO}_2$ (70)	383, 379
$\text{CHCl}=\text{CHCl}$	$\text{CHCl}_2\text{CHClNO}_2$ (67)	379
$\text{CHBr}=\text{CH}_2$	$\text{CHBrCH}_2\text{NO}_2$ (65)	379
$\text{CH}_2=\text{CH}_2$	$\text{CH}_3\text{CH}_2\text{NO}_2$ (50)	629
$\text{CH}_2=\text{CHCN}^\S$	$\text{O}_2\text{NCH}_2\text{CHCN}$ (76)	377, 380
$\text{CH}_2=\text{CHCN}^\dagger$	CH_3CHCHCN (14)	377
	$\text{O}_2\text{NCH}_2\text{CHCN}$ (25)	
	CH_3CHCHCN (16)	
	$\text{O}_2\text{NCH}=\text{CHCN}$ (48)	
	$\text{O}_2\text{NCH}_2\text{CHCH}_2\text{Cl}$ (61)	629
	$\text{CH}_3\text{CHCH}_2\text{NO}_2$ (40-47)	629, 630
	$\text{CH}_3\text{O}_2\text{CCHCH}_2\text{NO}_2$ (75)	377, 380, 631
	$\text{CH}_3\text{O}_2\text{CCHCH}_2\text{Cl}$ (7)	
	$\text{CH}_3\text{O}_2\text{CCHCHCH}_2\text{CH}(\text{OCOCCH}_3)\text{NO}_2$ (5-10)	
	1,2- and 1,4-Adducts and 1,2,3,4 bis adduct	
	$\text{C}_2\text{H}_5\text{CHCH}_2\text{NO}_2$ (47)	382
	$\text{CH}_3\text{CHCH}(\text{NO}_2)\text{CH}_2$ (25)	629
	$(\text{CH}_3)_2\text{CCH}_2\text{NO}_2$ (20-64)	630
	$n\text{-C}_3\text{H}_7\text{CHCH}_2\text{NO}_2$ (40)	629, 382, 630
		629

Note. References 385 to 631 are on pp 371-376


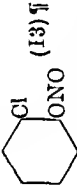
* The nitro alcohol is formed from the corresponding nitrite ester ($\text{CONO} \rightarrow \text{CONO}_2$) by hydrolysis, in working up the reaction mixture.

† No solvent was used.

‡ Ether was used as solvent.

in working up the

TABLE XIV—Continued
 B. Addition of Nitryl Chloride to Olefins and Acetylenes—Continued

Olefin	Product (%)	Refs.
$(\text{CH}_3)_2\text{CHCH}=\text{CH}_2$	$(\text{CH}_3)_2\text{CHCHClCH}_2\text{NO}_2$ (47)	629
$\text{C}_2\text{H}_5(\text{CH}_3)\text{C}=\text{CH}_2$	$(\text{CH}_3)_2\text{CHCHClCH}_2\text{Cl}$ (26) $\text{C}_2\text{H}_5(\text{CH}_3)\text{CClCH}_2\text{NO}_2$ (40)	629
	 (42)  (27)	
	 (13) ONO  (5) **	355, 630, 379
$n\text{-C}_4\text{H}_9\text{CH}=\text{CH}_2$	$n\text{-C}_4\text{H}_9\text{CHClCH}_2\text{NO}_2$ (42)	629
$n\text{-C}_3\text{H}_7(\text{CH}_3)\text{C}=\text{CH}_2$	$n\text{-C}_3\text{H}_7(\text{CH}_3)\text{CClCH}_2\text{NO}_2$ (35)	629
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}=\text{CH}_2$	$(\text{CH}_3)_2\text{CHCHClCH}_2\text{NO}_2$ (41)	629
$(\text{CH}_3)_2\text{C}=\text{CHOCOCCH}_3$	$(\text{CH}_3)_2\text{CClCHO}$ (21) $\dagger\dagger$	631
	$(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{CHO}$ (12)	
$n\text{-C}_5\text{H}_{11}\text{CH}=\text{CH}_2$	$n\text{-C}_5\text{H}_{11}\text{CHClCH}_2\text{NO}_2$ (39)	629
$\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	$\text{C}_6\text{H}_5\text{CCl}=\text{CHNO}_2$ (34)	369
	$\text{C}_6\text{H}_5\text{COCHCl}_2$ (9)	
	$\text{C}_6\text{H}_5\text{C}(\text{NO}_2)=\text{CHCl}$ (—)	383, 379
	$\text{C}_6\text{H}_5\text{C}(\text{NO}_2)_2\text{CHCl}_2$ (—)	
	$\text{C}_6\text{H}_5\text{CH}(\text{NO}_2)\text{CH}_2\text{Cl}$ (—)	379
	$\text{C}_6\text{H}_5\text{CH}(\text{NO}_2)\text{CHClCO}_2\text{H}$ (43)	383, 379
	$\text{C}_6\text{H}_5\text{COCH}_2\text{NO}_2$ (36) $\dagger\dagger$	631
	$\text{C}_6\text{H}_5\text{COCH}_2\text{Cl}$ (14)	
	$\text{C}_6\text{H}_5\text{COCH}(\text{NO}_2)\text{CH}_3$ (28)	631
	$\text{C}_6\text{H}_5\text{CHClCH}(\text{NO}_2)\text{C}_6\text{H}_5$ (27)	379

<i>C Addition of N₂O₄/X₂ to Olefins and Acetylenes</i>		
Olefin	Addendum	Product (%)
CHCl=CCl ₂	Cl ₂ /N ₂ O ₄	CCl ₂ CHClNO ₂ (5)
		CCl ₂ CHCl ₂ (2)
		CCl ₂ =CClNO ₂ (4)
		CCl ₂ CH ₂ NO ₂ (40)
CH ₂ =CCl ₂	Cl ₂ /N ₂ O ₄	CCl ₂ CH ₂ Cl (2)
		CCl ₂ CH ₂ NO ₂ (25)
	Br ₂ /N ₂ O ₄	CCl ₂ BrCH ₂ Br (9)
		CCl ₂ BrCH ₂ NO ₂ (7)
CHCl=CHCl	Cl ₂ /N ₂ O ₄	CHCl ₂ CHCl ₂ (3)
		CHCl ₂ CHClNO ₂ (41)
CH ₃ =CHBr	Cl ₂ /N ₂ O ₄	CH ₂ CHClCHBr (32)
		CHBr ₂ CH ₂ NO ₂ (35)
	Br ₂ /N ₂ O ₄	CH ₂ BrCHBr ₂ (58)
		CHCl ₂ CH ₂ NO ₂ (36)
CH ₃ =CHCl	Cl ₂ /N ₂ O ₄	CHClBrCH ₂ NO ₂ (28)
	Br ₂ /N ₂ O ₄	CHClBrCH ₂ Br (24)
		CHClCH ₂ NO ₂ (62)
CH ₂ =CHCN	I ₂ /N ₂ O ₄	CHNO ₂ =CHCN (25)
CH ₃ CH=CHCl	Cl ₂ /N ₂ O ₄	CH ₂ CH(NO ₂)CHCl ₂ (24)
CH ₃ CH=CH ₂	Cl ₂ /N ₂ O ₄	CH ₂ CH(NO ₂)CH ₂ Cl (14)
	Cl ₂ /N ₂ O ₄	CH ₂ CHClCH ₂ Cl (45)
	I ₂ /N ₂ O ₄	CH ₂ CHClCH ₂ NO ₂ (70)
CH ₂ =CHCO ₂ CH ₃	I ₂ /N ₂ O ₄	O ₂ NCH ₂ CHICO ₂ CH ₃ (75)



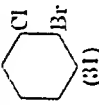
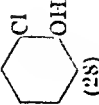
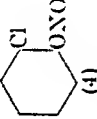
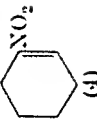
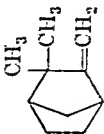
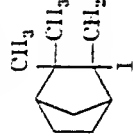
Note. References 385 to 631 are on pp 371-376.

§ This product was not isolated. After hydrolysis a mixture of about equal parts 1-chloro-2-cyclohexanol and 1-chloro-2-cyclohexyl nitrate was obtained.

** 1-Nitro-2-cyclohexanol was isolated.

†† These products were obtained after hydrolysis.

TABLE XIV—Continued
C. Addition of N_2O_4/N_2 to Olefins and Acetylenes—Continued

Olefin	Addendum	Product (%)	Refs.
$C_2H_5CH=CH_2$	Cl_2/N_2O_4 I_2/N_2O_4	$C_2H_5CH(NO_2)CH_2Cl$ (9) $C_2H_5CHClCH_2NO_2$ (62)	381 360
	$N_2O_4/BrCCl_3$	 (29)  (31)  (28)	358, 357
$CH_3C(OCOCH_3)=CHCH_3$	Cl_2/N_2O_4 Br_2/N_2O_4 I_2/N_2O_4	 (4)  (4) $CH_3COCHClCH_3$ (58) $CH_3COCHBrCH_3$ (50) $CH_3COCH_2CH_3$ (34) $CH_3COCOC_2H_5$ (23)	375 375 375
$C_6H_5C\equiv CH$	I_2/N_2O_4	$C_6H_5Cl=CHNO_2$ (86) (single isomer)	360
	I_2/N_2O_4	 (50)	360
$C_6H_5C\equiv CC_6H_5$	I_2/N_2O_4	$C_6H_5Cl=C(NO_2)C_6H_5$ <i>trans</i> (66) <i>cis</i> (15)	360
<i>trans</i> - $C_6H_5CH=CHC_6H_5$ <i>cis</i> - $C_6H_5CH=CHC_6H_5$	I_2/N_2O_4 I_2/N_2O_4	$C_6H_5CH(NO_2)CHClC_6H_5$ (96) ^{††} $C_6H_5CH(NO_2)CHIC_6H_5$ (63) ^{††}	360 360

Note: References 385 to 631 are on pp. 371–376.

^{††} The same adduct (a single isomer) was obtained from both *cis*- and *trans* stilbene. It is stated that it is probably the *erythro* isomer.

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